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UNIVERSITY OF ALBERTA

DEVELOPMENT OF A FILTRATION/ADSORPTION METHOD FOR DETERMINING OIL AND GREASE IN WASTEWATERS

by

Sandra Elizabeth Kok

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE
IN ENVIRONMENTAL ENGINEERING

DEPARTMENT OF CIVIL ENGINEERING

EDMONTON, ALBERTA
SPRING 1990

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Development of a Filtration/Adsorption Method for Determining Oil and Grease in Wastewaters submitted by Sandra Elizabeth Kok in partial fulfilment of the requirements for the degree of Master of Science in Environmental Engineering

(Supervisor)

James A. Plambeck

Date: April 10, 1990

ABSTRACT

Difficulties in monitoring for oil and grease in water and wastewaters include the following:

(i) objectives range from control of oil removal processes to assessing the biological effects of oil and grease;

(ii) the parameter is defined by the method; thus slight variations in the procedures create difficulties in comparing oil and grease values;

(iii) methods for determining oil and grease may not reflect the monitoring objective;

(iv) oil and grease is an umbrella term for many organics; the analytical method which is based on solvent extraction may exclude some of these organics or may include others that do not cause the problems associated with oil and grease;

(v) oil and grease may be present in both dissolved and suspended form; however, none of the present standard methods differentiate between the two forms.

The most common method for determining oil and grease in water and wastewater is the partition-gravimetric method which consists of solvent extraction of the oil and grease, solvent evaporation and gravimetric determination. This method cannot be reliably used for low concentrations of oil and grease (< 25 mg/L).

The objectives of this thesis were to provide an overview of the problems associated with oil and grease in water and wastewaters (i.e. sources, types and fate, monitoring needs, sampling, analytical procedures) and to review the suitability of potential alternatives to the partition-gravimetric method. An analytical protocol termed the "filtration/adsorption column method" was developed to improve the accuracy of quantifying the oil and grease in wastewater by gravimetry.

The filtration/adsorption method (described herein as a "dual column method") consisted of a diatomaceous earth column to capture suspended oil followed by an XAD-2 resin column to capture dissolved oil. Synthetic wastewaters (dispersions of hexadecane and naphthalene), and actual wastewaters (oilfield brines), were tested. The oil and grease content was obtained by soxhlet extraction of the columns with dichloromethane, solvent evaporation and gravimetry. The results indicated that the dual column method was more accurate and reproducible than the partition-gravimetric method for the synthetic dispersions. For one oilfield brine, the partition-gravimetric method was slightly more reproducible than the dual column method. For another oilfield brine, the oil was in dissolved form and only the dual column method was appropriate. Overall, the dual column method is favored because of advantages in sampling, ease of the method and its ability to distinguish between dispersed and dissolved oil and grease.

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The author of this thesis would like to acknowledge the assistance provided to her by her supervisor, Dr. Steve Hrudey, and the patience of her dear friend, Keith Lue.

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1 INTRODUCTION

Oil and grease is a water quality parameter, meant to describe hydrophobic ("water-hating") organic compounds present in water. These hydrophobic organic compounds may be insoluble or have very low solubilities in water. Depending on the concentration of oil and grease in the water or wastewater, the oil and grease may be present as a combination of a floating oil layer, fine or large suspended droplets or a dissolved portion. Each type of oil and grease can pose problems in the control of oil and grease in the environment.

Oil and grease in water and wastewater originates from animal and vegetable products and petroleum-based products. The widespread use of such products results in considerable mass discharges of oil and grease into the environment. For example, Hunter and Heukelian (1965) estimated that in municipal wastewaters, a high percent (20%) of the particulate matter constitutes oil and grease. Discharges of petroleum products into the marine environment from tankers, marine oil spills, offshore oil production and land-based operations (refineries, storm runoff, industrial wastes, automotive wastes and municipal wastes) are estimated at 1.9 - 11.4 million tonnes/year (Connell, 1984). Depending on its source, physical nature, chemical constituents and concentration, the negative effects may include aesthetic problems caused by floating layers of oil and grease, reduction of oxygen levels in receiving streams, operational problems in wastewater treatment plants, and impairment of organisms. Therefore, oil and grease is an important wastewater component to control.

Exercising control on oil and grease requires effective monitoring capabilities. However, there are several problems associated with proper monitoring of oil and grease in water. These problems stem from the numerous reasons for monitoring oil and grease in water, the wide range of organic compounds that are collectively grouped under the term "oil and grease", the various physical ways in which oil and grease may be present and the inability of the current standard methods to encompass all these factors.

2 RESEARCH OBJECTIVES

The objectives of this thesis are:

(1) to present an overview of the sources, types and fate of oil and grease in water

(2) to review current legislation regarding the discharge of oil and grease in the environment

(3) to identify monitoring needs for oil and grease at low concentrations

(4) to assess present techniques for sampling oil and grease containing waters

(5) to review analytical procedures for determining oil and grease in waters

(6) to review the suitability of analytical methods used to determine low concentrations of organics in water for oil and grease analysis, and

(7) to develop and evaluate an analytical protocol, referred to as the **filtration/adsorption method** (referred to as the dual column method), which was developed (a) to improve the accuracy of the gravimetric method for quantifying oil and grease at low concentrations in water and (b) to isolate the dispersed and dissolved fractions of oil and grease in water.

LITERATURE REVIEW

3 SOURCES OF OIL AND GREASE IN WASTEWATER

Oil and grease in wastewater is derived from animal and vegetable sources or petroleum-derived sources. In municipal wastewater, the oil and grease components are derived from both sources, with the contributions of each source depending on the industrial and domestic inputs. Industrial wastewaters at the point of generation generally contain relatively high levels of oil and grease which may require reduction prior to discharge into a municipal sewer or receiving waters.

Table 1 highlights the wide variety of sources of oil and grease containing wastewaters and the range of concentrations encountered. Food processing wastewaters generally have high concentrations of oil and grease, as reflected in the upper value of 4 000 mg/L for an edible fat and oils processing plant. Metal cutting/grinding/degreasing operations produce wastewaters having a wide range of oil and grease concentrations (20 to 9 000 mg/L). The concentration of oil and grease in domestic sewage ranges from 50 to 100 mg/L while that for petroleum refineries range from 20 to 140 mg/L.

3.1 Animal and Vegetable Derived Oil and Grease

Animal and vegetable oil and grease are present in food from meat, dairy, poultry, fish, nuts and processed food oils. Hence, the main sources of animal and vegetable oil and

TABLE 1. TYPICAL SOURCES AND CONCENTRATIONS OF OIL AND GREASE IN WASTEWATER

SOURCE	CONCENTRATION (average or range) mg/L	REFERENCE
poultry processing	100 - 400	Env. Canada, 1981
edible fats and oils	4 000	Env. Canada, 1979
shrimp processing	115	Env. Canada, 1979
petroleum refining	21 - 144	Snider and Manning, 1982
washrack degreasing	20 - 8 700	Huang, 1984
metal working	30 - 440	Kang and Lawrence, 1984
metal cutting	70 - 186	Lopez and Johnston, 1981
industrial laundry	1 100	Van Gils et al., 1984
municipal sewage	50 - 100	Loehr, 1969

grease in wastewaters are the food processing industry and domestic discharges (i.e. households and restaurants).

3.1.1 Origin and composition

The oil and grease from animal and vegetable matter is comprised of fatty acids, triglycerides and phosphoglycerides, which are part of a group of biomolecules known as lipids. The fats and oils are present mostly as triglycerides. Since the fatty acid part ($RCOO^-$) of the triglyceride molecule comprises a larger mass fraction (94-96% of the total weight of the molecule) compared to the glycerol group (C_3H_5), the nature of the triglyceride is dictated by the properties of the fatty acid component.

Table 2 lists the more common fatty acids and triglycerides and specific origins of animal and vegetable oil and grease.

3.1.2 Environmentally relevant properties of animal and vegetable oil and grease

Environmentally relevant properties refer to those properties of the oil and grease components which negatively affect wastewater treatment operations or the receiving waters into which the wastewater discharges.

The most relevant property of animal and vegetable oil and grease in wastewater treatment is the melting point. Many of the triglycerides have melting points above 25°C (e.g. the most common, stearic and palmitic acids, are solids at temperatures above 25°C). Therefore, at operating temperatures for sewers and

TABLE 2. PROPERTIES AND SOURCES OF FATTY ACIDS - ORIGIN OF ANIMAL AND VEGETABLE OIL AND GREASE

FATTY ACID	NO. OF C ATOMS	MOL. WT. TRIGLYCERIDE	MELTING POINT, °C	SOURCE
Saturated				
Butyric	4	302.4	-8	milk
Caproic	6	386.5	-3.4	milk, coconut
Caprolic	8	470.7	16.7	seeds
Capric	10	554.8	31.6	milk, seeds
Lauric	12	639.0	44.2	coconut, palm kernel
Myristic	14	723.1	54.4	most animal/vegetable
Palmitic	16	807.3	62.9	most animal/vegetable, lard, tallow
Stearic	18	891.5	69.6	most vegetable oils, lard, tallow, butter
Unsaturated				
Caprolic	10	548.8		milk
Lauroleic	12	632.9		milk
Myristoleic	14	717.1		milk
Palmitoleic	16	717.1		milk, beef fat
Oleic	18	879.3	14,16	olive oil, pecan oil, most animal/vegetable
Elaidic	18	879.3	44	beef fat, animal
Linoleic	18	879.3	-5	safflower, sunflower

Adapted from Severn, 1979.

wastewater treatment processes, the greases are present as solid or semi-solids.

The semi-solid and solid nature of these greases created problems in early sewage treatment plant operations. The main problems were blinding of screens, interference with the operation of Imhoff tank, activated sludge and digestion processes, and clogged filters (Gehm, 1953). Since then, these operational problems have been lessened considerably, because of pretreatment of industrial wastewater at the point of generation, and improvements in the design and operation of sewage treatment plants (Loehr, 1982). Specific changes include the use of grease traps along the sewer system to minimize congealing of the suspended grease and consequent plugging of pipes. Proper design also allows for larger pipe diameters, use of pipes with very smooth surfaces, provision for heating of pipes and placement of cleanout plugs. The float skimmings (obtained from the settling tanks) that is sent to the anaerobic digesters used to be the cause of scum buildup, and cleanout at regular intervals was required. This problem has since been eliminated through the installation of heaters and mixers which facilitate biodegradation of the greases.

Uncontrolled discharges of high concentrations of vegetable oil and grease lead to rapid depletion of oxygen in receiving waters. This oxygen depletion occurs because of its consumption by microorganisms in the receiving environment. Subsequently, the dissolved oxygen concentration in the receiving water may decrease to levels that cannot sustain higher organisms.

3.2 Petroleum-Derived Oil and Grease

Petroleum-derived oil and grease is obtained from many sources including on-shore and offshore crude oil recovery operations, petroleum refineries, coal processing, tar sands processing, organic chemical manufacturing, metal cutting and grinding operations.

3.2.1 Origin and composition

The petroleum-derived oil and grease are generally considered to be hydrocarbons (i.e. compounds containing only carbon and hydrogen only). These hydrocarbons comprise (i) aliphatics (straight chain, branched or cyclic) and (ii) aromatic hydrocarbons ranging from monocyclic compounds (benzene and its derivatives) to large polynuclear molecules such as benzo(a)pyrene as shown in Figure 1. Also present in crude oil are non-hydrocarbon materials containing nitrogen, oxygen and sulfur and metalloporphyrins. These compounds may also be present in these types of petroleum-based wastewaters.

3.2.2 Environmentally relevant properties of petroleum hydrocarbons

Table 3 lists hydrocarbons typically found in petroleum refinery wastewaters, and their environmentally-relevant chemical properties. These compounds are also found in other petroleum-based wastewaters, however, their relative concentrations will vary. As shown in Table 3,

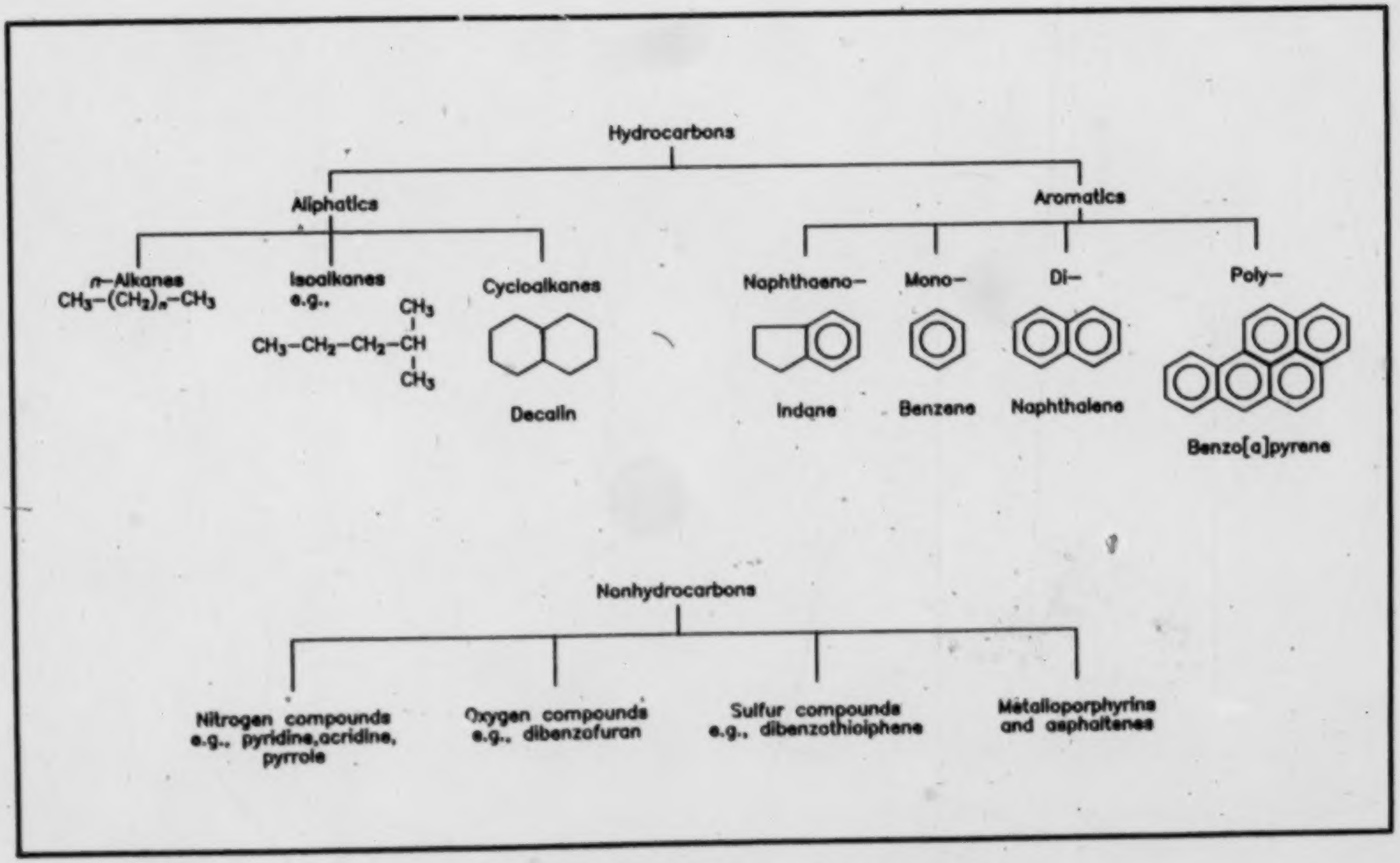

Hydrocarbons
Aliphatics
Aromatics
n-Alkanes
CH3-(CH2)n-CH3
Isoalkanes
e.g.,
CH3-CH2-CH2-CH(CH3)-CH3
Cycloalkanes
Decalin
Naphthaeno-
Indane
Mono-
Benzene
Di-
Naphthalene
Poly-
Benzo[a]pyrene
Nonhydrocarbons
Nitrogen compounds
e.g., pyridine,acridine,
pyrrole
Oxygen compounds
e.g., dibenzofuran
Sulfur compounds
e.g., dibenzothiophene
Metalloporphyrins
and asphaltenes

FIGURE 1: CHEMICAL COMPONENTS OF PETROLEUM

Adapted from Connell and Martin, 1984.

TABLE 3. ENVIRONMENTALLY RELEVANT PROPERTIES OF HYDROCARBONS FOUND IN PETROLEUM-TYPE WASTEWATERS

COMPOUND	MOL. WT.	SOLUBILITY IN WATER	log K_{ow}	HENRY'S LAW CONSTANT
n-Alkanes				
Hexane	86	9.5		
Octane	114	0.66		7.89×10^{-4}
Dodecane	170	0.0037		
Tetradecane	198	0.0022		
Hexadecane	226	0.0009		
Octadecane	255	0.0021		
Alkylated Benzenes				
Toluene	92	534.8		
Ethyl benzene	106	161.2		
o-Xylene	106	170.5		
m-Xylene	106	146.0		
p-Xylene	106	156.0		
1,3,5-Trimethyl benzene		59.0		
n-Butyl benzene	134	11.8		
Naphthalene	128	31.7	3.36	4.84×10^{-3}
1-Methyl naphthalene	142	28.5		
Ethyl naphthalene	156	10.7		
1,3- Dimethyl naphthalene	156	8.0		
Polynuclear Aromatics				
Phenanthrene	178	1.29	4.57	3.93×10^{-5}
Anthracene	178	0.073	4.54	
2-Methyl anthracene	192	0.261		
Fluorene	166	1.98	4.47	
Acenapthene	154	3.93	4.03	1.46×10^{-4}
Biphenyl		7.0		4.08×10^{-3}
Pyrene	202	0.135	5.18	
Chrysene	228	0.002	5.91	

Notes :
Mol. Wt. - molecular weight
Solubility - in water, units in mg/L
Henry's Law constant - units in $m^3atm.gmole^{-1}$
log K_{ow} - octanol - water partition coefficient

References:
Solubility data - MacKay and Shiu, 1977
- Jordan and Payne, 1980
log K_{ow} data - Walters and Luthy, 1984
Henry's Law data - MacKay, Shiu and Sutherland, 1979

there is a wide range of chemical compounds of widely differing nature.

The most important environmentally relevant chemical properties are solubility, volatility and partitioning character. Solubility is the ability of the hydrocarbon to dissolve in water. Therefore, solubility reflects the tendency of a compound to persist in the aqueous phase. Volatility represents the ability of the hydrocarbon to leave the aqueous phase, and is represented by the Henry's law coefficient, H. Partitioning represents the equilibrium distribution of the hydrocarbon between water and an immiscible organic phase. This factor is correlated with the tendency of the hydrocarbon to accumulate in biological tissues, and is determined by the octanol-water coefficient (log K_{ow}) (this value is the logarithm of the ratio of the solubility of the hydrocarbon in octanol to its solubility in water).

Water soluble hydrocarbons are more available for rapid uptake by organisms than insoluble hydrocarbons. As shown in Table 3, the solubility of the hydrocarbons range from less than 1 µg/L for long chain alkanes such as hexadecane, to up to 535 mg/L for low molecular weight aromatic compounds such as toluene.

The Henry's law constants vary substantially. Compounds such as naphthalene and biphenyl have relatively high degrees of volatilization (e.g. H for naphthalene is 4.84×10^{-3} atm. $gmole^{-1}$, while that for biphenyl is

3.93×10^{-3} atm. $gmole^{-1}$). Other compounds such as phenanthrene and acenapthene have lower volatilities, as indicated by H values one or two orders of magnitude less than naphthalene and biphenyl.

The octanol-water partition coefficient is correlated to the degree to which an organic compound will partition between the tissue of an organism and the water phase. For naphthalene, the log K_{ow} is 3.36. By comparison, the K_{ow} values for the polynuclear aromatics are 1-2 orders of magnitude greater indicating that the latter compounds are more likely to be absorbed in biological tissue.

The properties discussed above are also important in the collection and analysis of samples for oil and grease determination. The marginal solubilities exhibited by many of the hydrocarbons means that the effect of environmental conditions such as changes in temperature may result in changes in the physical nature (i.e. dissolved to insoluble). Losses during sampling and analysis can occur because of the volatile nature of some of the constituents. The log K_{ow} may also be used to reflect the ease of dissolution of the hydrocarbon in the solvent. Hence, appropriate precautions in sampling are required as discussed in Section 6. In addition, the wide range of chemical properties associated with the various classes of compounds leads to limitations in any analytical method which is meant to represent all of the hydrocarbons as discussed in Section 7.

3.2.3 Biological effects of petroleum hydrocarbons

The combined properties described in 3.2.2 may result in negative effects to organisms. These effects of petroleum hydrocarbons to organisms can be classified under (i) acute lethal toxicity over a short time period brought about by discharge of a toxic substance (e.g. spills) or treatment of an area with a toxic material on a single occasion and (ii) sublethal toxicity brought about by exposure over a longer time period on a continuous or intermittent basis (Connell and Miller, 1984).

Lethal effects result in the death of the organism. Petroleum hydrocarbons can cause death in organisms through (i) coating and subsequent asphyxiation, (ii) contact poisoning and (iii) exposure to water soluble components. Sublethal effects do not result in immediate or death in the short term but are manifested by erosion of gill epithelia and destruction of mucous cells, damage to chemical senses, immobilization of sperm, reduced fertilization rates and death of fertile eggs (Côté, citing various researchers, 1974).

Both lethal and sublethal effects caused by petroleum hydrocarbons have been extensively reviewed by Connell and Martin, 1984. The water soluble fraction (WSF) or water accommodated fraction (WAF) of the petroleum hydrocarbons are considerably more toxic to organisms than the alkane (water-insoluble) fraction. The water-accommodated fraction refers to the hydrocarbons that are soluble and which may also be present as microdroplets in the water phase. Table 4 shows

TABLE 4. TOXICITIES OF SOLUBLE AROMATICS TO CLASSES OF MARINE ORGANISMS

	ESTIMATED RANGES OF LETHAL CONCENTRATIONS OF SOLUBLE AROMATICS (ppm)		
CLASS OF ORGANISM		Crude Oils (96 h LC_{50})	No. 2 Fuel Oil
Flora	10 - 100	ID[1]	ID
Finfish	5 - 50	1 - >50	1 - >10
Crustaceans	1 - 10	1 - >10	1 - >10
Bivalves	5 - 50	1 - >10	0.1 - >10
Gastropods	1 - 100	1 - >10	0.5[2]- >5
Other benthic invertebrates	1 - 10	>5 - 10	>1
Larvae (all species)	0.1 - 1	0.1 - 5	
Juveniles	--	5 - >10	1 - 10

Notes: [1]inadequate data
[2]-tentative result

Adapted from Connell and Martin, 1984, citing Miller, 1982.

lethal toxicity concentrations of soluble aromatic compounds to aquatic organisms. The 96 h LC_{50} represents the concentration at which 50% of the fish in a 96 hour bioassay test are killed. Fuel oil is generally more toxic than crude oil for most organisms. The lethal concentrations of soluble aromatics range from 0.1 to >10 ppm. It should be noted that regulations generally call for the 96 h toxicity test for monitoring of treated effluents. Burks (1980) has found that refinery effluents (after activated sludge treatment) were non-toxic to fathead minnows for a 96 h test. However, in long term exposure tests (up to 32 days), total mortality of the fish was experienced in five of seven tests conducted. This finding is significant in assessing the long term fate of oil and grease discharges.

Sublethal effects are more difficult to determine than acute lethal effects, and therefore, there are many contradictions in the literature. It appears however that sublethal concentrations range from less than 10 µg/L to over 1000 µg/L for soluble aromatic compounds. Changes in behavioral patterns occur at the lower end of the concentration range while disturbances in growth and reproduction occur at the higher concentration ranges. Marine molluscs experienced sublethal effects (depressed rates of feeding, reduced absorption efficiency, increased respiration and decreased growth) at concentrations of 30 - 750 µg/L of water accomodated hydrocarbons (Bayne et. al, 1981)

In addition to their environmental persistence, petroleum hydrocarbons may cause impairment in the flavour of fish flesh, and taste and odor problems in drinking water (Bailey, 1979 citing USEPA, 1975).

3.2.4 Monitoring needs for biological assessment studies involving petroleum hydrocarbons

Extremely low levels of petroleum hydrocarbons have been found to affect organisms. In many of these studies, the concentration of hydrocarbon is deduced from a known input of crude oil in a known study volume of water. The losses of the oil caused by adherence to glassware are generally not accounted for. Actual confirmation of the concentration of the prepared water sample by sampling and analysis is usually not done.

The term "water accommodated" is meant to reflect the possibility of both insoluble and soluble oil which could affect the organism. Distinction between both portions would be desirable as the mechanisms for biological uptake are different.

Monitoring needs in this area of research therefore must take into account these considerations to allow more meaningful interpretation of results.

3.2.5 Comparison between the different types of oil and grease

The environmental effects of petroleum-based oil and grease centre mostly around the fate of these compounds to organisms at relatively low concentrations. Compared to the relatively more biodegradable animal and vegetable derived oil and grease, the petroleum hydrocarbons may persist over long periods of time.

The biodegradability of the two types of oil and grease can be compared using the biological oxygen demand (BOD) parameter. This parameter is a measure of the amount of oxygen consumed by a bacterial culture over a fixed time period (usually 5 days). The BOD therefore indicates the level of uptake of the pollutant achievable. Table 5 shows relative BOD values for various food and petroleum-based oils. A high value signifies that the substrate is relatively biodegradable. These data show that the food oils are more biodegradable than the petroleum based oils.

TABLE 5. BIODEGRADABILITY OF FOOD OILS AND PETROLEUM-BASED OILS

TYPE OF OIL	BIODEGRADABILITY (measured as BOD[1])
Food Oils	
Butterfat	1.79
Coconut Oil	1.77
Corn Oil	1.88
Herring oil	1.71
Palm oil	2.00
Petroleum-Based Oils	
Fuel oil	0.98
Machine oil	0.29
Mineral oil	0.31

Note: [1] - BOD: g BOD_5 per gram of oil tested (BOD_5 : 5-day biochemical oxygen demand)

Adapted from Loehr, 1985.

4 TREATMENT PROCESSES FOR THE REMOVAL OF OIL AND GREASE IN WASTEWATERS

Treatment processes for removing oil and grease from wastewater may be classified into three categories based on the level of oil concentrations desired in the effluent prior to discharge: (i) primary, (ii) secondary and (iii) tertiary. For most cases, secondary treatment is the maximum degree of treatment used prior to discharge of the final effluent into the municipal sewer or receiving waters. Tertiary treatment processes are used primarily where recycling of wastewater is practised and the concentrations of oil and grease must be substantially reduced.

4.1 Primary Treatment Processes

Primary methods remove large grease particles and readily separable oil and grease components. Examples of primary treatment methods are screening and gravity settling.

4.1.1 Screening

Screening for removal of gross solids, including grease solids involves sieving of the wastewater through parallel rods, bars or wires, grating, wire mesh or perforated plates. Screens are usually designated as coarse (> 5 mm openings) or fine (<5 mm openings). Screening of the wastewater prevents plugging of pumps and piping.

4.1.2 Gravity settling

In gravity settling, separation of the oil and grease occurs because of the difference in density between the lighter oil and grease and the heavier water. The oil and grease forms a separate top layer which is skimmed off and disposed of. Figure 2 shows a typical gravity separator used for oil removal.

4.2 Secondary Treatment Processes

In secondary treatment processes, further removal of the oil and grease is achieved using gas flotation, biological treatment or other physical-chemical processes.

4.2.1 Gas flotation

Gas flotation involves the addition of gas bubbles to the wastewater. The gas bubbles adhere to the particulate oil and grease and other suspended solids and cause the oil and grease to be carried to the surface of the wastewater, where the resultant float layer can be skimmed off.

There are two types of flotation systems: induced gas flotation and dissolved air flotation. The main difference between two systems is the mode by which the gas bubbles are generated. In induced gas flotation, as shown in Figure 3, the bubbles are generated using rotors which draw air into a central chamber, from which it is mechanically forced by rotor action to form gas bubbles of diameters ranging from 50 to 70 µm.

In dissolved air flotation, as shown in Figure 4, the wastewater is pressurized to 400 kPa and then released into a tank at atmospheric pressure. The reduction in pressure causes the dissolved air to come out of solution, forming bubbles which attach to the oil and grease particles, as well as suspended

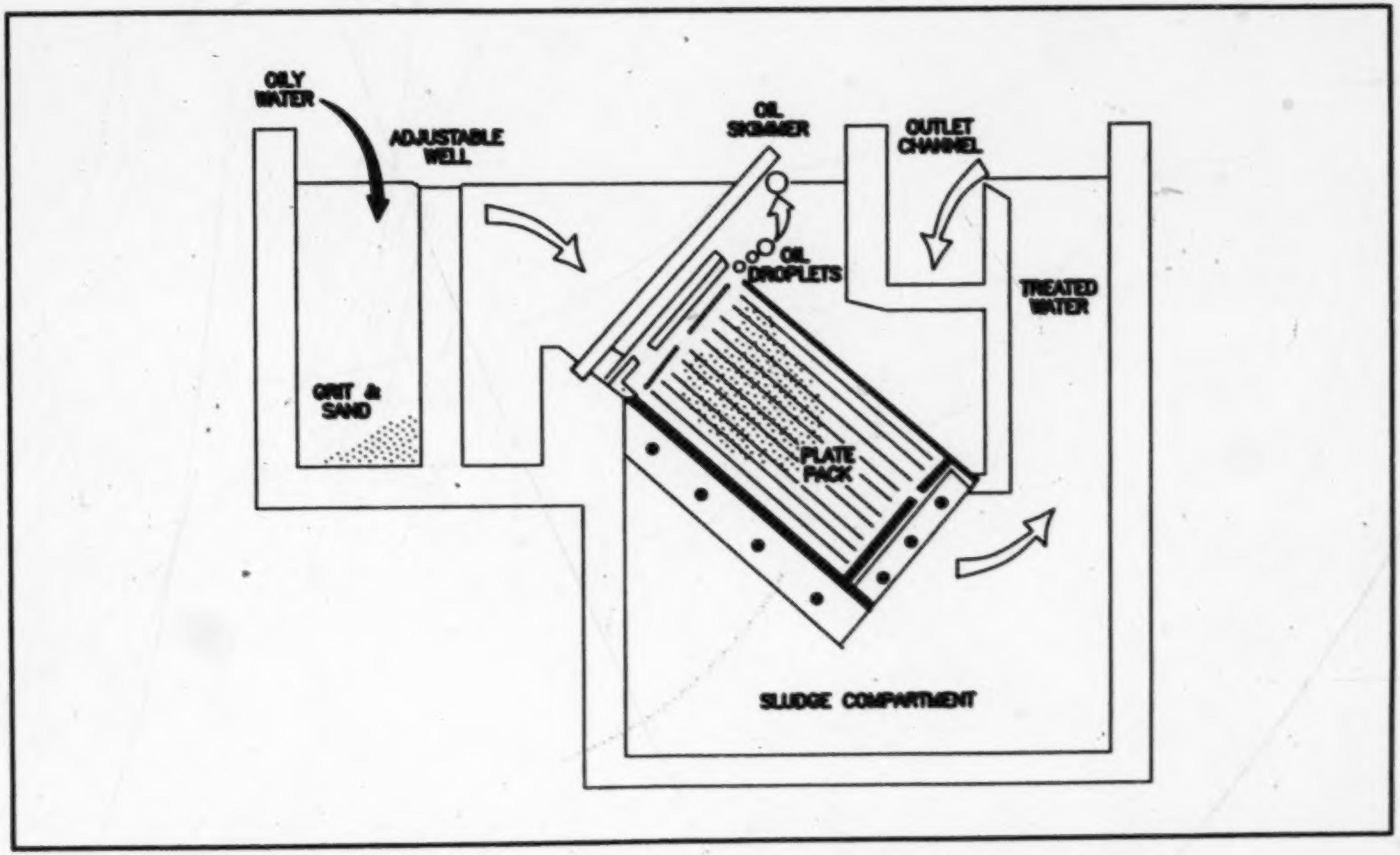
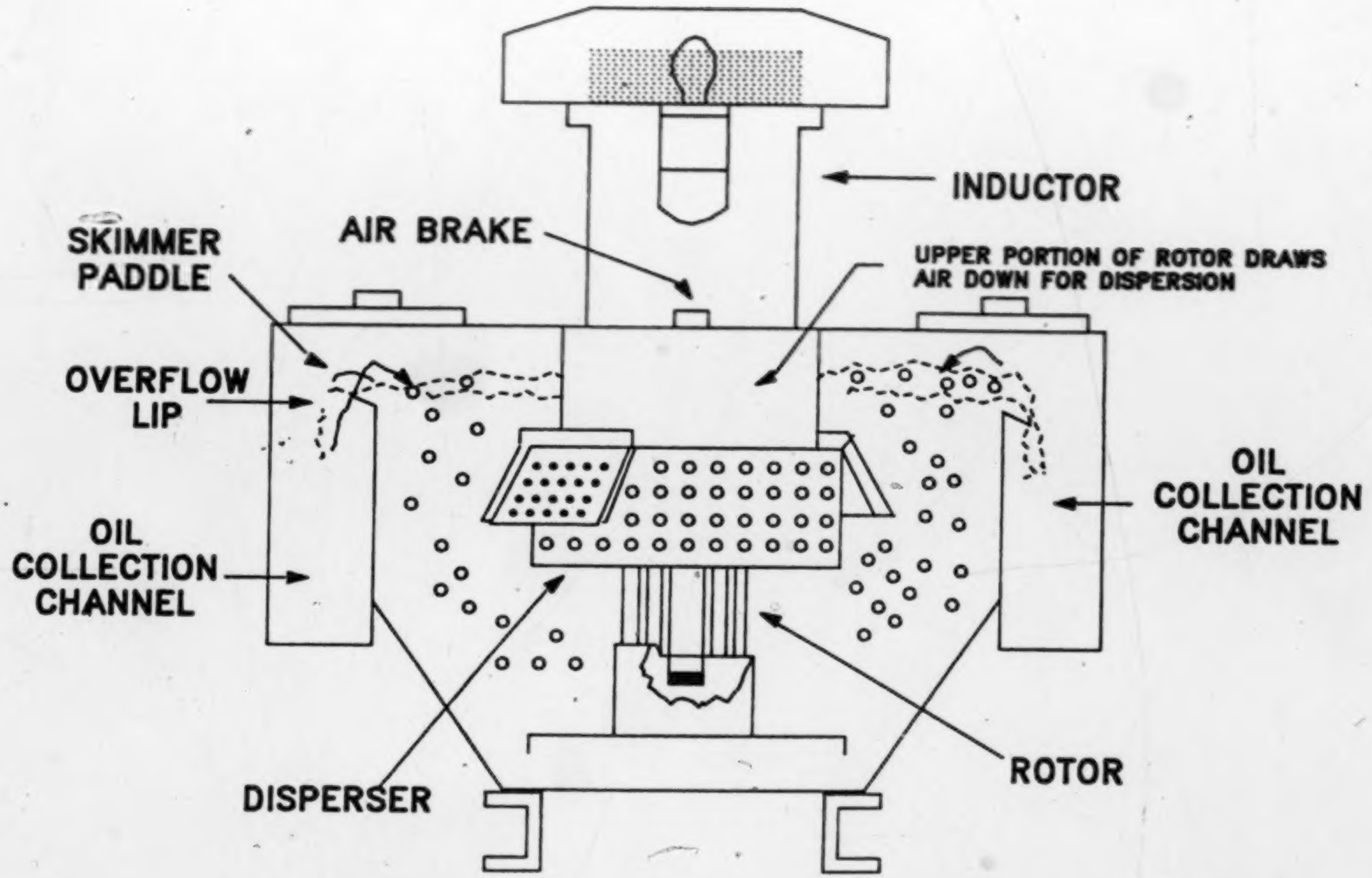

OILY WATER
ADJUSTABLE WELL
GRIT & SAND
OIL SKIMMER
OIL DROPLETS
OUTLET CHANNEL
TREATED WATER
PLATE PACK
SLUDGE COMPARTMENT

FIGURE 2: SCHEMATIC OF A GRAVITY SEPARATION PROCESS WITH CORRUGATED PLATE INTERCEPTORS

Adapted from Environment Canada, 1983.


INDUCTOR
AIR BRAKE
SKIMMER PADDLE
UPPER PORTION OF ROTOR DRAWS AIR DOWN FOR DISPERSION
OVERFLOW LIP
OIL COLLECTION CHANNEL
OIL COLLECTION CHANNEL
DISPERSER
ROTOR

SCHEMATIC OF INDUCED GAS FLOTATION PROCESS

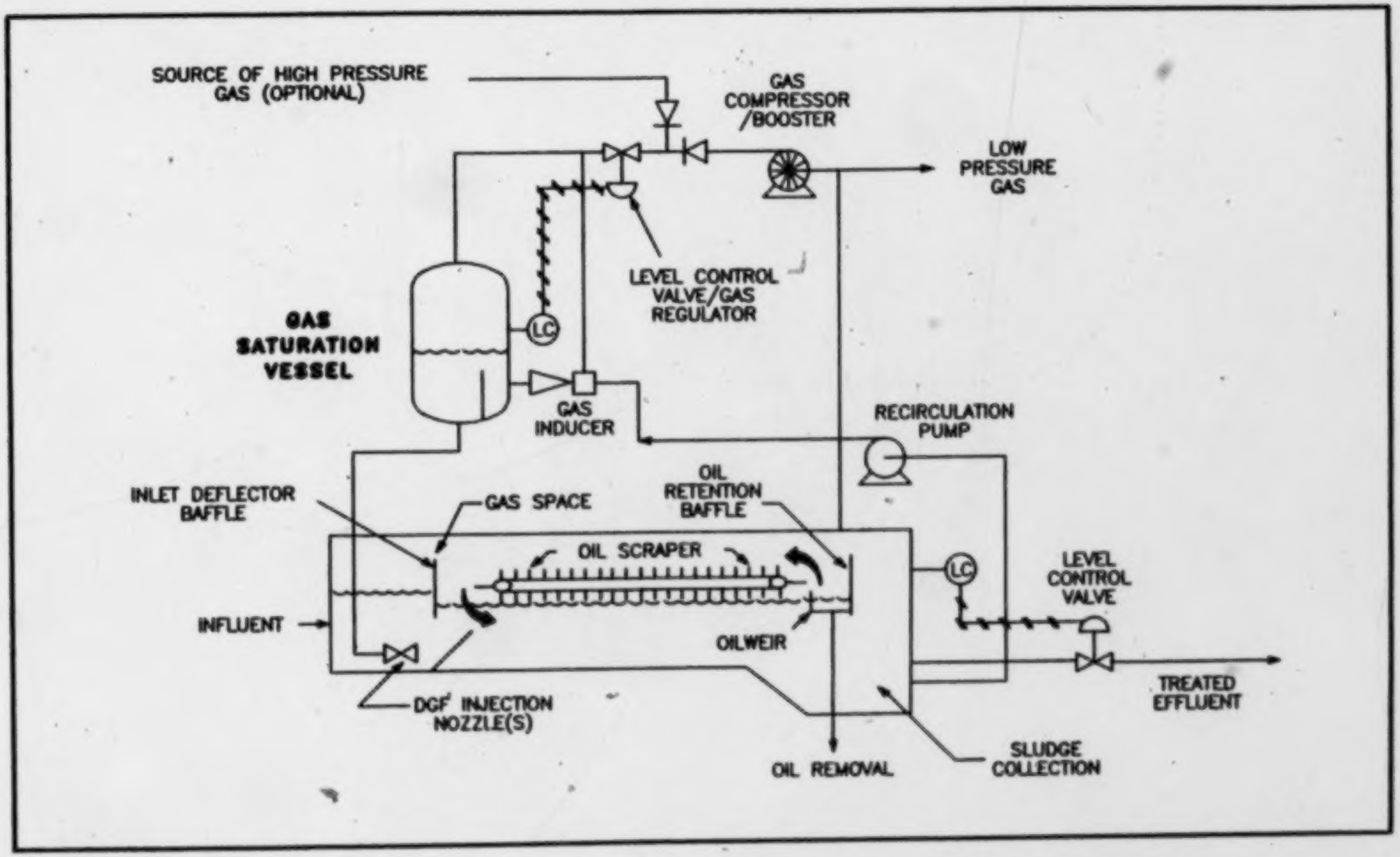

SOURCE OF HIGH PRESSURE GAS (OPTIONAL)
GAS COMPRESSOR /BOOSTER
LOW PRESSURE GAS
LEVEL CONTROL VALVE/GAS REGULATOR
GAS SATURATION VESSEL
LC
GAS INDUCER
RECIRCULATION PUMP
INLET DEFLECTOR BAFFLE
GAS SPACE
OIL RETENTION BAFFLE
OIL SCRAPER
LC
LEVEL CONTROL VALVE
INFLUENT
OILWEIR
TREATED EFFLUENT
DGF[1] INJECTION NOZZLE(S)
OIL REMOVAL
SLUDGE COLLECTION

FIGURE 4: SCHEMATIC OF DISSOLVED GAS FLOTATION PROCESS

material in the wastewater. The oil and grease then coalesce at the top of the unit, forming a separate float layer which is then skimmed off. The gas bubbles generated in dissolved air flotation are much finer than those formed in induced gas flotation systems.

4.2.2 Biological treatment

Biological treatment relies on bacteria to use the oil and grease components as substrate for their growth, thereby reducing the oil and grease concentration in the wastewater. Biological treatment systems include activated sludge treatment, aeration lagoons, and oxidation ditches, as well as anaerobic systems.

4.3 Tertiary Treatment Processes

In some cases, polishing of the wastewater is required such as in wastewater recycling applications or prior to discharge into receiving waters. Tertiary or polishing treatment processes include granular media filtration and membrane processes.

4.3.1 Granular media filtration

Granular media filtration is used for removing traces of oil and grease in wastewater. It involves passage of the wastewater through a bed of media such as sand or anthracite, as shown in Figure 5. The oil droplets (as well as other suspended matter) are trapped on the surface of the media resulting in

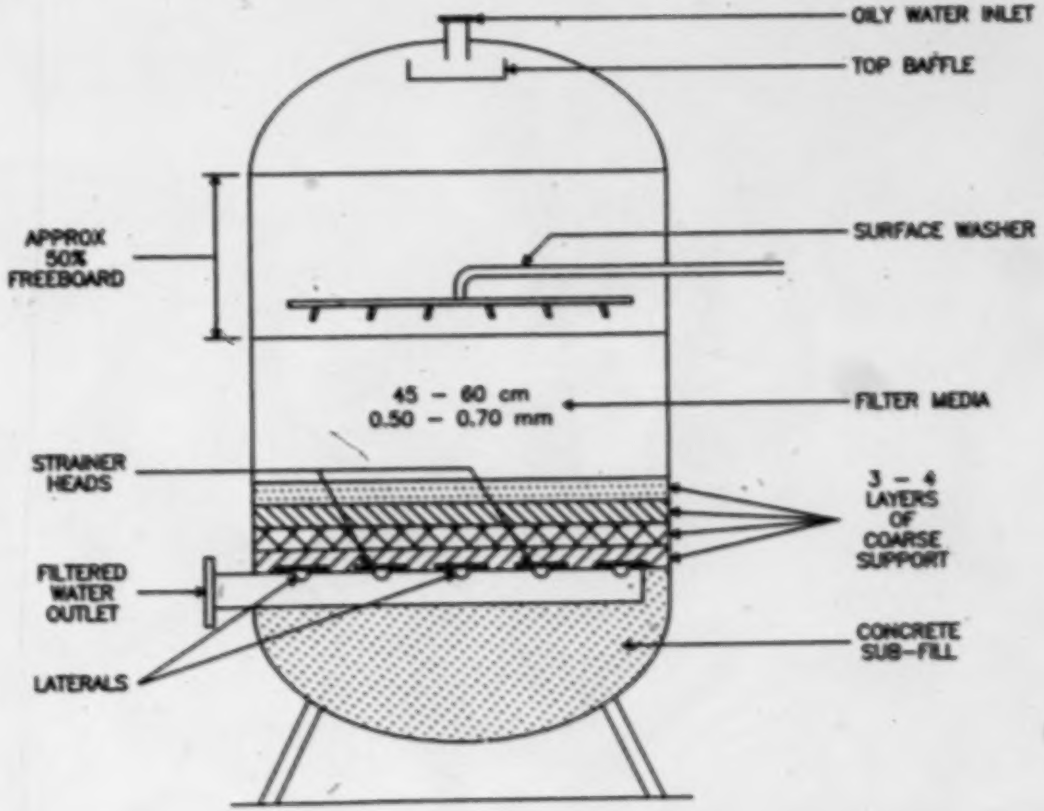

OILY WATER INLET
TOP BAFFLE
APPROX 50% FREEBOARD
SURFACE WASHER
45 – 60 cm
0.50 – 0.70 mm
FILTER MEDIA
STRAINER HEADS
3 – 4 LAYERS OF COARSE SUPPORT
FILTERED WATER OUTLET
CONCRETE SUB-FILL
LATERALS

FIGURE 5: SCHEMATIC OF A GRANULAR MEDIA FILTER

further reduction of the oil and grease concentration in the wastewater.

4.3.2 Membrane processes

Membrane processes, such as crossflow microfiltration and ultrafiltration, involve the use of porous membranes (inorganic or polymeric) which do not allow passage of the suspended oil particles. The wastewater is fed tangential to the surface of the membrane, as shown in Figure 6, and the filtrate passes through the membrane under the pumping pressure provided. The oil and suspended particles are concentrated in the exiting reject stream.

4.4 Selection of Oil Removal Process

The specific processes used depend on the particular process streams being treated. Generally, food processing operations discharging into municipal sewers have gravity settlers, as a minimum. Refinery operations usually have secondary treatment (biological treatment) prior to discharge into either the municipal sewer or receiving waters.

4.5 Monitoring Requirements for Oil Removal Processes

The oil removal processes discussed in Sections 4.1 - 4.3 remove undissolved oil. Table 6 shows typical oil and grease concentrations achieved by oil removal processes. Screening achieves a level of 50 mg/L for a poultry processing effluent while flotation of an edible oil-type wastewater produces an effluent having 50 mg/L. For treatment systems processing

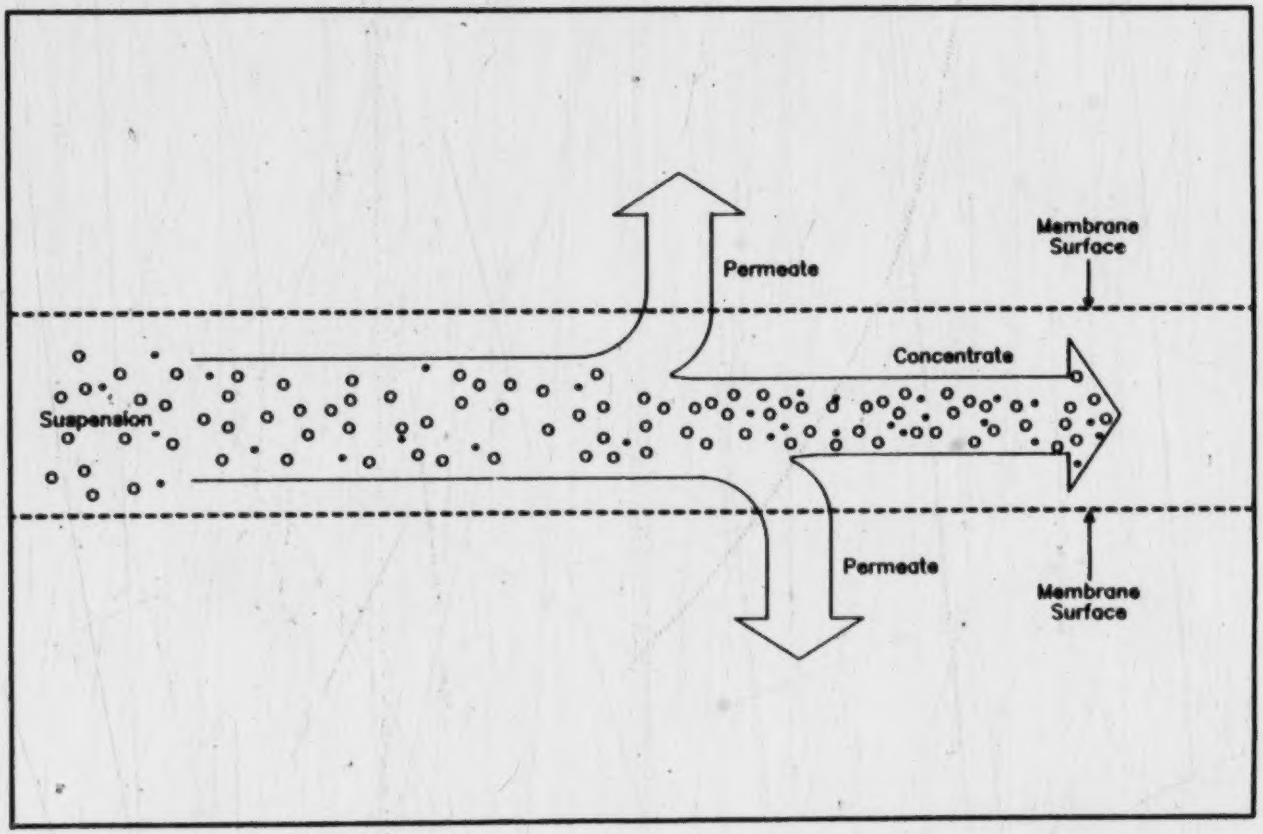

Permeate
Membrane Surface
Concentrate
Suspension
Permeate
Membrane Surface

FIGURE 6: SCHEMATIC OF CROSSFLOW MICROFILTRATION AND ULTRAFILTRATION PROCESSES

TABLE 6. OIL AND GREASE CONCENTRATIONS IN WASTEWATER TREATMENT EFFLUENTS

INDUSTRY	TREATMENT PROCESS	CONCENTRATION (mg/L)		REFERENCE
		in	out	
poultry processing	screening	600	50	Env. Canada, 1979
edible oils and fats	flotation		50	"
tuna cannery	flotation		40-70	"
petroleum refinery	DAF	24	<10	EPA, 1978
	AS/FC		<10	"
	filtration		<10	"
	API separator		20-200	EPA, 1974
	DAF		5-20	"
	filtration		6-20	"
Municipal	Activated sludge	69	1.3	Snider, 1982
		53	3.6	"
		20	4.3	"

Notes: DAF - dissolved air flotation
AS/FC - activated sludge/final clarifier

petroleum refinery wastewater, the concentrations in the final effluents range from 5 to 20 mg/L for most processes except the API separator, and trickling filters. With the polishing type processes (granular media filtration) the oil and grease concentration will be skewed towards the lower end of the range. Oil and grease concentrations in final municipal effluents have been measured at concentrations less than 5 mg/L.

Monitoring needs for oil removal processes must cover a range from below 5 mg/L to up to several thousand mg/L for undissolved oil. However, note that the values shown in Table 6 reflect total oil and grease, rather than undissolved or suspended oil and grease. The total oil and grease concentrations represent the oil removal process only if the concentration of suspended (or undissolved) fraction is relatively high compared with the dissolved fraction. Wastewaters having a high proportion of insoluble hydrocarbons (as previously discussed in Section 3) and fatty acids can generally be classified as such. However, other petroleum-based wastewaters such as oilfield wastewater from oil drilling operations and petroleum refineries may contain relatively high concentrations of dissolved hydrocarbons. Because these dissolved hydrocarbons are not removed in the conventional oil removal processes previously discussed, the oil and grease values obtained by the standard analytical procedures will be misleading. Therefore, there is a need to distinguish between the soluble and insoluble fractions of oil and grease, particularly in process effluents where the concentration of the dispersed oil may be low compared to the dissolved oil.

5 REGULATIONS GOVERNING THE DISCHARGE OF OIL AND GREASE IN WASTEWATERS

Existing regulations or guidelines governing the discharge of oil and grease in wastewaters cover (i) discharge into municipal sewers and (ii) discharge in waterways, such as rivers, lakes and seas. The discharge limits are usually set as allowable waste loading per unit production, e.g. kg (oil and grease)/m^3-d oil production. The allowable waste loading is calculated on the basis of the average concentrations of oil and grease achievable by existing best practical treatment technology and average waste volumes generated. Therefore, the net discharge of oil and grease to the receiving water or municipal sewer is also a function of the wastewater volumes generated. While the concentration may be high, if the relative volume of wastewater discharge is low, then the environmental impact may not be as severe as with high volumes/low concentrations of oil and grease.

Table 7 lists the concentrations of oil and grease on which selected regulations and guidelines are based for an assortment of wastewater discharges. For discharge into municipal sewers, both types of oil and grease (animal/vegetable and petroleum) are considered, as reflected by the difference in the allowable concentration. The more readily biodegradable animal and vegetable oil and grease can be discharged at much higher levels than petroleum and mineral oil and grease as exemplified in the Alberta guidelines (300 mg/L for the former, 100 mg/L for the latter).

TABLE 7. LEGISLATION GOVERNING OIL AND GREASE DISCHARGES

LOCATION	TYPE OF LEGISLATION	WASTEWATER TYPE	ALLOWABLE CONC. OF OIL AND GREASE mg/L	RECEIVING SYSTEM	REFERENCE
Alberta	guidelines	animal mineral or petroleum	300 100	municipal sewer	Alberta Environment, 1978
Alberta	guidelines	petroleum refinery storm runoff	10	receiving watercourse	Alberta Environment, 1978
Calgary, Alberta	regulations	industrial	450	municipal sewer	City of Calgary Sewer Regulations,
British Columbia (1979)	guidelines	mining, smelting and related industry	15	receiving watercourse	Eco-Log, 1988
Quebec (1981)	regulation	petroleum refinery	10	receiving watercourse	Eco-Log, 1988
Canada (1974)	guidelines	domestic	15	receiving watercourse	Environment Canada, 1974
United Kingdom	target	offshore oil production water	40	ocean	Pitre, 1984
United States	regulation	offshore oil production water	42	ocean	Pitre, 1984

Allowable concentrations for oil and grease into receiving waterways are considerably lower (10 to 40 mg/L) than that for discharge into municipal sewers. For most discharges, the emphasis in the regulation has traditionally been the prevention of a visible sheen, caused by floating oil. For waters containing less than 10 mg/L (as may be found with refinery storm runoff), the regulations usually consider this water to be free of oil and grease, because of the inability of the standard method of analysis to be sufficiently reliable (Env. Can., 1976). Thus, there is a need to improve the lower detection ability of the standard methods for determining oil and grease in order for this parameter to be of more utility in developing guidelines and regulations for oil and grease discharges in wastewaters.

6 SAMPLING OF OIL AND GREASE CONTAINING WATERS

The first step in the determination of oil and grease in water is the collection of a representative sample. Sampling protocols for oil and grease must consider the following:

(i) the nature of the sample and the sampling location
(ii) the time and frequency of sampling
(iii) sample volume
(iv) preservation

6.1 Nature of the Sample and the Sampling Environment

Oil and grease in wastewater exists in various forms: (i) an insoluble floating layer, (ii) dispersed droplets of varying diameters having a certain distribution in the wastewater, and (iii) dissolved. The relative contribution of each form depends on: (i) the concentration of oil and grease in the sample and (ii) the degree of turbulence at the point of interest. The insoluble fraction causes difficulties in the collection of a representative sample as separation and upward flow of the insoluble oil result in concentration profiles with depth as shown in Figure 7. There is usually a distinct separable oil layer at the surface (coalesced oil), a more concentrated oil water layer directly below the surface (cream layer) and another region where the oil droplets are more evenly dispersed as an oil in water emulsion.

Ideal conditions for sampling for oil and grease require turbulent flow conditions (Reynolds number > 3000),

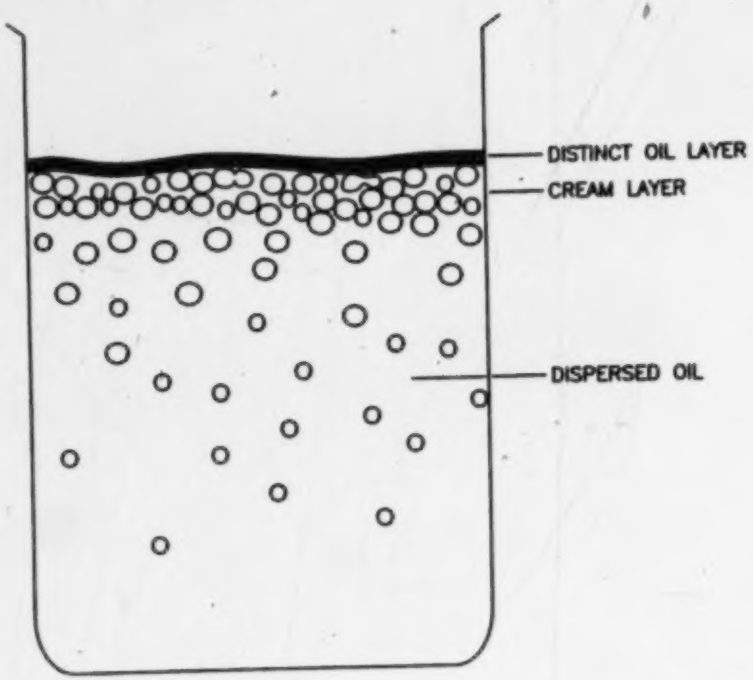

DISTINCT OIL LAYER
CREAM LAYER
DISPERSED OIL

FIGURE 7: CONCENTRATION PROFILE OF OIL AND GREASE IN WATER

corresponding to a velocity of at least 0.6 m/s so that oil and grease droplets would be well mixed in the water. For laminar flow, (Reynolds number <3000) considerable distance from the point of discharge (equivalent to 10 times the pipe diameter) is recommended for the sampling location, so that adequate time for mixing can occur. For turbulent flow, the sample location could be located at a shorter distance (at least three pipe diameters downstream). Withdrawal from a closed pipe at a distance at least one-third of the pipe diameter is also recommended so that a representative sample is collected. The above recommendations for sampling are by Palmer, 1980.

These flow conditions may be met in continuous oil removal processes where the effluents are transported in closed pipes and suitable sampling ports are installed. Regular flushing of the sampling lines is necessary to ensure that deposits accumulated in the lines are cleaned. However, in many cases, the recommended flow conditions are rarely met. For example, in a survey of sampling methods for refinery effluents, 25 out of the 29 respondents did not meet the velocity criteria. Most of the samples were collected (16 out of 25) from open channels (CONCAWE, 1980), where turbulent conditions did not exist. It should be noted that many of these conditions are typical of effluent monitoring locations used for regulation reporting purposes.

Solubility changes occurring as a result of drop in temperature may make sampling inhomogenous because of the solidification of components. In open channels, volatilization of the compounds having relatively high Henry's law constant also occur causing reduced oil and grease concentrations.

In studies assessing the biological impact of water accomodated oils, the samples are usually withdrawn from below the water surface. The main concern in the collection of such samples is preventing the surface oil from sticking to the sides of the sampling vessel and contaminating the sample. Many automatic samplers are available for withdrawing subsurface samples. McAuliffe (1987) and CONCAWE (1980) have reviewed the basic operations of these sampling devices. Mechanical automatic samplers involve the use of cups that dip into the water and are mounted on a chain for transport. The samples could either be composited or kept as discrete samples. Suction lift collection methods apply a vacuum to suck the sample into a container. Discrete sampling methods (as provided by the mechanical and suction systems) allow only a limited number of samples to be taken in a given time. Pumping of the sample is sometimes used to pump the sample into an appropriate container. The automatic samplers allow collection of large sample volumes over a short period of time with flow rates up to 60 L/min being available.

6.2 Time and Frequency of Sampling

Samples may be either (i) grab or discrete, (ii) composite or (iii) continuous. In grab samples, a discrete volume of water is sampled at one instant. Composite samples comprise of several batch samples collected at different times and mixed together to provide an average concentration. For oil and grease samples, obtaining composite samples by combining batch samples is not a good practice because of losses that can occur during handling and transferring. Continuous sampling is generally used for on-line monitoring of the oil and grease as later described in Section 8 for certain applications.

The frequency of sampling should be such that the concentration of the oil and grease reflects typical conditions of plant discharges as well as upset conditions. For oil and grease containing waters, Palmer (1980) recommended that a 24-h automatic composite sample be taken, backed up by regular grab samples. Grab samples allow the determination of the concentration at a particular time and tracing of operational problems. Composite samples provide an average concentration and do not generally show cyclic variations in the concentration. The collection of composite samples is most appropriate in oil removal processes where they can be taken in proportion to the flow rate of the effluent. Discrete samples are generally taken from rivers, lakes and end-of-pipe situations. Discrete sample collection for oil and grease is the most common way of sampling.

6.3 Sample Volume

The volume of sample collected depends on the concentration and the analytical method being used. For oil analysis, Palmer recommended that the minimum volume for an oil content of 25 mg/L or more should be 1 L if the standard partition gravimetric method (see Section 7) is used. Larger sample volumes are, therefore, desirable for concentrations below 25 mg/L.

6.4 Sample Preservation

Sample preservation for oil and grease determination consists of acidification to pH 2 and storage at 4°C. Acidification and cooling inhibit the biodegradation of the oil and grease. Many of the petroleum hydrocarbons are readily oxidized through light-catalyzed reactions and bacterial action. The alkanes are readily oxidized to form hydroperoxides, secondary alcohols, ketones and organic acids (Malins, 1980). The non-substituted and alkyl-substituted aromatic hydrocarbons degrade to form catechols (Gibson, 1977, Karrick, 1977 and Hopper, 1978, as cited by Malins, 1980).

Table 8 shows a comparison of oil and grease analyses conducted in the field and in the laboratory using the partition-infrared method (see Section 7). The results indicated that considerable losses were suffered. Most of the losses were attributed to losses caused by the oil sticking to the sample containers. However, no rigorous work was done to verify this source of loss.

6.5 Sample Splitting

In sample splitting, a large sample volume is divided into several portions, thereby allowing intercomparison of

TABLE 8. COMPARISON OF FIELD AND LABORATORY OIL AND GREASE ANALYSES

SAMPLE	OIL AND GREASE CONCENTRATION[1] mg/L	
	Field	Lab
Dillon No. 1	21.0	9.0
Dillon No. 2	23.8	7.5
Dillon No. 3	16.4	---
Average	20.4	8.3
Std. deviation	3.7	1.1
Relative std. deviation	18.1	13.3
Shell No. 1	17.2	5.3
Shell No. 2	13.2	13.0
Shell No. 3	12.8	17.8
Average	14.4	12.0
Std. deviation	2.4	6.3
Relative std. deviation	16.7	52.5

Note : [1]-using partition-infrared method (see Section 7)

Adapted from Rewick et al., 1981.

analysis to be conducted with the same sample. However, for oil and grease analysis, the losses of insoluble oil that may occur during handling and transfer may introduce too much error to allow the objectives of sample splitting to be met.

6.6 Summary of Problems Related to the Sampling of Oil and Grease Containing Waters

There are many factors which make collection of a representative sample of oil and grease difficult. These include (i) the losses caused by absorption of insoluble oil to glassware and solids and sediments, (ii) inaccessibility of proper sampling locations and difficulty in obtaining good mixing.

At relatively high oil concentrations, the difficulty is compounded by stratification of the various oil and grease fractions with the suspended and free floating oil and grease fractions and the layering effect. With lower oil concentrations, volatilization of components may cause significant losses during sampling. Finely emulsified oil droplets losses caused by adsorption of the dispersed oil onto glassware may cause larger errors compared to more concentrated samples.

7 ANALYTICAL PROCEDURES FOR THE DETERMINATION OF OIL AND GREASE IN WATER

This section discusses (i) the historical development of methods for determining oil and grease in water (ii) the current standard methods and a comparison of these methods, (iii) alternative methods investigated for oil and grease analysis and (iv) information gaps in the methods used.

7.1 Development of the Analysis of Oil and Grease in Water

The need for determining oil and grease in water stemmed from difficulties encountered in sewage treatment plant operations, as discussed in Section 3.1.

The first-recorded method for oil and grease determination was developed by Hazen in 1892 (as cited by Hatfield and Symons, 1945).

Hazen's method involved evaporating a 500 mL sample of sewage to 50 mL followed by acidification with hydrochloric acid, evaporation to dryness and extraction of the oil and grease with ether using a soxhlet extractor. Subsequently, the solvent was evaporated and the residue was weighed to produce a value for the oil and grease. This method was time-consuming and required as much as two days to perform the analysis. Reproducibility of the analysis was also poor.

Ludwig (1941) developed an alternative procedure which involved acidification of a 500 or 1000 mL sample with hydrochloric acid, boiling for approximately 15 minutes to allow the fats and oils to form as a surface layer, and cooling overnight to allow the grease to solidify or form a viscous mass.

Subsequent filtration, drying of the residue, soxhlet extraction, solvent evaporation and weighing of the residue yielded the oil and grease concentration. This procedure was developed to enhance separation of the oil and grease from the sample.

Okun et al. (1941) developed a method similar to that of Ludwig, with the main difference being a slight change in filtration. To aid in capturing the suspended grease particles, a grease-free cotton disc was placed on top of the filter paper both of which were fitted in a perforated aluminum dish to facilitate its removal after filtration of the sample.

In 1945, Hatfield and Symons reviewed several proposed methods for selecting a standard procedure. They recommended that the Okun and Ludwig methods be combined and therefore this was incorporated as the standard method. However, the Okun/Ludwig method required up to 25 hours to complete and hence, there was still a need to reduce the analytical time requirements.

Pomeroy (1941) identified the main shortcomings of Ludwig's method as

(i) excessive losses of greases during sample drying
(ii) reversion of fatty acids to insoluble soaps during sample drying
(iii) production of ether-soluble matter
(iv) insolubilizing of oils by oxidation and polymerization
(v) extraction of nongreases

Pomeroy found that losses of grease during drying amounted to as high as 25 percent of the original grease in the sample. These losses were determined by mixing samples of grease separated from sewage skimmings with 500 mL of water and drying the mixture on a hot plate, in accordance with Ludwig's procedure.

Sample drying also caused the fatty acids (formed upon acidification with hydrochloric acid) to revert back to insoluble (in organic solvent) soap
according to the equation (1):

$$2RCOOH + CaCl2 \longleftrightarrow 2CaCOOR + 2HCl \quad \text{..... equation (1)}$$

Such losses amounted to 34 percent of the original weight of the fatty acids obtained from sewer grease. These losses were determined by mixing calcium chloride dihydrate and the fatty acids obtained from sewer grease samples with ether and water in a dish, and evaporating the mixture to dryness.

Production of ether-soluble matter during acidification can occur with food substances that do not contribute to the operational problems associated with oil and grease in treatment processes. Pomeroy cited phospholipide lecithin as an example. Phospholipide lecithin is found in egg yolk and other foods, and is a chemically combined fat which do not impart greasy characteristics to the wastewater. However, acidification of the wastewater sample results in the fatty acid form of the phospholipide. Subsequently, this would increase the final value of the oil and grease. Tests conducted with egg yolk showed that this reaction resulted in an increase in the value of the oil and grease by 28%, compared to that obtained with a non-acidified sample.

Precipitation of the oils by oxidation could occur over the lengthy drying time (24 hours or more) required for the evaporation of the sewage. Tests showed that the formation of these insoluble oils by oxidation amounted to up to 27 percent loss in hexane soluble materials in grease samples collected from a raw sludge sample.

The extraction of non-greases in petroleum ether was also identified by previous researchers (Pomeroy, citing Knechtges, Peterson and Strong, 1934) who reported 6 to 21 per cent of ash in the solvent extracts. This ash was attributed to the dissolving of inorganic salts by petroleum ether. Pomeroy felt that other materials likely to dissolve in the organic solvents would include organic acids, amine salts, sugars, gums, resins, rubber, hydrocarbons of the naphthalene type, solid chlorinated hydrocarbons and sulfur. The presence of 0.25 and 0.3 percent of nitrogen in the ash samples of Knechtges, Peterson and Strong supported Pomeroy's view.

Pomeroy then developed the wet method which was based on practices used in the petroleum industry for the determination of oil in oilfield wastewater. The wet method eliminated the need for boiling of the sample where the losses caused by volatilization and oxidation (by conversion to insoluble material), and reversal of fatty acids into insoluble fatty acid soaps were considerable. The wet method accounted for both emulsion-forming samples (such as sludges) and liquid samples. The present standard partition-gravimetric method (see Section 7.2) is based on the latter.

Pomeroy's method for emulsion-forming wastewaters involved acidification with 5 mL of 50% sulphuric acid, liquid-liquid extraction of the sample in a separatory funnel (for sample volumes less than 1000 mL) or in the sample bottle for sample volumes larger than 1000 mL. The entire solvent/water mixture was then transferred to a round bottomed flask connected to a reflux condenser. The round bottom flask and its contents were heated in a water bath maintained at 90 - 100°C to facilitate breaking of the emulsion by heat. Particular care was taken to boil only the water phase. After boiling, the phases were cooled. The solvent which was the upper layer was pipetted into a tared conical flask. The solvent was then evaporated using a steam or water bath at a temperature below 100 C. Residual vapours after solvent evaporation were displaced using a stream of dry air or gas. The flask was then dried at 100 to 105 C for 20 minutes, then cooled in a dessicator for no more than 3 hours. The dried, cooled flask was then weighed and the value of the oil and grease determined.

For other samples where emulsions were not formed, the procedure consisted of extraction of the oil and grease using a separatory funnel, allowing the mixture to stand for 30 minutes and then removing the lower aqueous layer into another separatory funnel where another extraction was done. If a difficult-to-break emulsion formed, and separation of the layers was difficult, continuation of the procedure using the above-described method using heat treatment, was recommended. Successive extractions of the sample with 50 mL volumes of solvent were conducted. A total of 3 to 4 extractions was found to be sufficient.

Pomeroy carried out experiments on a wide range of samples (screened and unscreened sewage, sewage sludge, meat processing wastewater, fish cannery waste, milk samples, and oilfield wastewater). The oil and grease concentrations obtained with these samples ranged from 31 to 17 100 mg/L.

Reproducibility of the method as shown by the results of several repeats was good, with less than 3% difference from the mean obtained for the majority of samples. Results of interlaboratory analyses using both modes of extraction also showed good agreement.

Comparison of results with the standard method (using hexane as solvent and liquid samples having concentrations ranging from less than 100 mg/L to sludge samples having concentrations of about 17 000 mg/L) showed that the wet method produced higher values in all cases than the Ludwig method. The difference was greatest for the screened sewage samples (concentration was < 200 mg/L), with 18 to 61% higher values being obtained. A 7-12 percent difference was observed for the sludge samples.

Pomeroy also highlighted the problems associated with the use of different solvents. At that time, Standard Methods allowed the use of petroleum ether, ethyl ether or chloroform. The difference in the results when ethyl ether, isopropyl ether, benzene and chloroform were used was found to be insignificant for most samples tested (sewage, sewage sludge, meat packing and fish cannery wastewater). However, these solvents gave slightly higher results than the standard hexane, or petroleum ether for the wastewaters tested (except for oilfield wastewater). Hexane produced a higher result than benzene (89 vs 71 mg/L) for the oilfield type wastewater.

Gilcreas, Sanderson and Elmer (1953) found that the heat treatment of the sample as proposed by Pomeroy (1941) did not break the emulsions created with their samples. Instead of heat, anhydrous sodium sulphate was found to be most reliable for breaking the emulsion. They also found that in some samples, up to seven extractions with the solvent were required. Actual results of these tests were not reported.

They also developed a semi-wet extraction method where the boiling and cooling steps of the standard method of Okun/Ludwig were eliminated. Instead, the filter paper and diatomaceous earth collected after filtration of the sample was simply transferred to a flask. Solvent was then added to the flask containing the filter paper and diatomaceous earth, and the contents were mixed using a glass stirrer. The solvent was then poured off and collected in a 300 mL distilling flask. The process of adding more solvent, stirring and pouring it off was repeated 9 times.

Tests were also conducted with a procedure developed by Sanderson, in which the boiling and freezing steps of the standard method were eliminated. The sample was simply filtered through diatomaceous earth and Whatman No. 40 filter paper underlain with a muslin cloth. The soxhlet extraction procedure was shortened to 4 hours and the rate of extraction was increased from 7 cycles/h to 20 cycles/h. Petroleum ether was the solvent used.

Although the semi-wet method was operationally simpler and required less time, an extensive study involving several laboratories indicated that the Sanderson method was more reliable. The main drawback of the semi-wet method was the uncertainty of complete extraction of greases in the solvent.

The Sanderson method is still used today and is known as the soxhlet extraction method.

Developments since 1953 to the method for determination of oil and grease have focused on (i) solvent choice, (ii) emulsion breaking, (iii) increasing the detection limit of the wet method and (iv) distinguishing between petroleum type oil and grease and that derived from animal and vegetable sources.

Chanin (1968) introduced the use of 1,1,2-trichlorotrifluoroethane (freon 113) as an alternative solvent to hexane which had been the standard solvent. The advantages of freon compared to hexane was its nonflammability, which made it safer for handling in the laboratory. The boiling point of freon is lower than that of hexane (48°C vs 69°C). Chanin tested freon using the wet extraction procedure and the soxhlet extraction procedure (using hexane) for sewage samples. The average concentration obtained with the freon/wet extraction method was 97.7 mg/L while that for the hexane/soxhlet extraction was 110 mg/L. Recoveries of oil obtained when the wastewater was spiked with a mixture of a known oil and grease produced an average percent recovery for the freon/wet extraction method of 94.3 and 94.5 for the hexane/soxhlet extraction method.

Tests using dispersions of representative oil and greases (lard, SAE 30 oil, olive oil) demonstrated that for the light oils (SAE 30 and olive oil) the wet extraction method provided better recoveries. For SAE 30 oil, the average recovery using the hexane/soxhlet extraction method was 88.2% while for the freon/wet extraction method, the average recovery was 94.5%. With olive oil, the hexane/soxhlet extraction method produced an average recovery of only 38.8% compared to 109.1% for the freon/wet extraction method presumably, because of the inability of the filter aid to retain the olive oil, which was the lightest oil tested. Based on this work, the use of freon was incorporated into the Standard Method for oil and grease determination.

Some wastewaters are highly emulsified or tend to form emulsions during solvent extraction using a separatory funnel. The emulsions result from the presence of fine solids and surfactants. Surfactants, when combined with oil lead to the formation of very fine droplets. This decreases contact between the solvent and the oil and hence solvent extraction is not as efficient. Vigorous shaking enhances the formation of emulsions of the immiscible solvent phase with the water phase, resulting in a stable middle layer that takes a long time to separate.

Fine solids, such as clays, form a thin skin around the oil droplets. Contact between the solvent and the oil droplet is difficult as the thin film must be penetrated. Some petroleum products such as asphaltenes and resins also produce a similar effect as clay.

Sodium chloride has been found to prevent the formation of these stable middle emulsion layers during solvent extraction. Taras and Blum (1968) added 5% w/w of sodium chloride to metal cutting wastewater samples. The standard wet extraction method was used, with freon as the solvent. Recoveries ranged for 84 to 100% for samples spiked with lubricating oils, compared to recoveries obtained when no salt was used. Gruenfeld (1975) also obtained improvements in extraction efficiency when sodium chloride was used in prepared dispersions of crude oil in water. Gruenfeld also found that sulphuric acid also produced higher extraction efficiencies.

The addition of salts such as sodium chloride aids in breaking these emulsions by neutralizing the electrical charge on the oil droplets, thereby facilitating coalescence and separation into separate phases. The acid converts surface active materials such as sodium carboxylates (which are present in petroleum type wastewaters) to their protonated form which do not have as high a surface active property. Despite the use of salt and acid, stubborn emulsions may still form and alternative methods such as the Soxhlet extraction method must be used.

The need for differentiating between the oil and grease from animal and vegetable sources and that from petroleum was recognized by Ullmann and Sanderson as early as 1959. They used a chromatographic separation technique for separating the two types of oil and grease dissolved in the petroleum ether extract. The extracts were passed through alumina adsorption columns which selectively extracted the polar vegetable fats and oils, leaving the non-polar petroleum hydrocarbons in the solvent. Two solvents, petroleum ether and n-hexane were also evaluated. The total oil and grease concentrations in the sewage samples tested ranged from 82 to 139 mg/L. The upper limit of the method was also tested and found to be about 650 mg/L.

The increasing importance of the fate of petroleum oil and greases at low concentrations to organisms and the effects of oil spills in marine environments created a need to monitor oil and grease at very low concentrations. Gruenfeld (1973) tested the use of infrared spectrophotometry for quantification of such concentrations of oil and grease in petroleum based wastewaters. The infrared method was thereafter, incorporated as a standard method. It should however, be noted that this method had been proposed by Simard in 1949.

7.2 Present Standard Methods for the Determination of Oil and Grease in Water

The wet extraction method, the soxhlet extraction method and the infrared method survive today as the standard methods currently used for measuring oil and grease in water. The wet extraction method is known as the partition-gravimetric method.

7.2.1 Partition-gravimetric method

The partition-gravimetric method is used for liquid samples. The procedure recommended by Standard Methods, Method

503A, (APHA, 1985) is described here. A 1-litre sample is acidified to pH 2 with concentrated hydrochloric acid (50 w/w). After acidification, the oil and grease components are then extracted into an organic solvent by liquid-liquid extraction by manually shaking a separatory funnel for about 2 minutes for each volume of solvent used. Where emulsions are likely to be created through the vigorous shaking of the sample during liquid-liquid extraction in the separatory funnel, longer (up to 5 minutes) but more gentle shaking is recommended. Three 30 mL serial extractions with freon are used. Each solvent volume is passed through a Whatman No. 40 filter containing anhydrous sodium sulphate which dries the solvent of entrained or dissolved water. The solvent is collected in a tared 125 mL round bottom flask. A final rinse of the filter paper with 10 mL of solvent is then carried out. The freon solvent containing the oil and grease components is then evaporated using a water bath at 70°C. The flask containing the residue is then weighed. By subtraction of the weight of the flask and residue and the empty flask, the value of the oil and grease concentration is determined.

The main advantage of the partition-gravimetric method is that it is a relatively simple procedure, requiring standard laboratory equipment. However, there are some serious limitations of the partition-gravimetric method as described below. These limitations are:

(i) need for acidification
(ii) choice of solvent
(iii) formation of emulsions

(iv) evaporative losses

(v) tedious operation

(vi) detection limit

7.2.1.1 Need for acidification. The original reason for acid addition for oil and grease analysis was to convert fatty acids found in the animal and vegetable oil and grease, into their protonated form as previously shown in Equation 1. However, for certain petroleum-based wastewaters, the use of acidification is questionable since water-soluble, low molecular weight organic acids, converted to their undissociated form would be extracted in the solvent, leading to a higher value of the oil and grease. For example, oil and grease values for non-acidified versus acidified effluents from a flotation process treating an oilfield waste water were 7.6 and 26.3 mg/L respectively; for another sample, the corresponding values were 36.3 and 61.8 mg/L respectively (Jackson, 1981). Therefore, higher values obtained using acidified samples would not represent the true removal efficiency of free oil by the oil removal process.

Later reasons for acid addition were sample preservation (see Section 6) and emulsion-breaking (see Section 7.1). Therefore, the benefits of preservation versus the potential higher values caused by acidification for petroleum-based samples must be carefully weighed. For example, if samples are analyzed immediately, acid addition may not be necessary, since biodegradation of the oil and grease components would be minimal. Alternatively confirmation studies on the biodegradability of the sample should be conducted.

7.2.1.2 Choice of solvent. The organic solvents generally considered for oil and grease are mostly non-polar, which is most suitable for dissolving the oil and grease components (i.e. the insoluble, non-polar organics). However, there will be some tendency for the organic solvents to dissolve polar organic compounds, depending on the ease of solubility of these compounds.

Freon 113 (1,1,2-trichlorotrifluoroethane) has been designated in Standard Methods as the standard solvent for the oil and grease analysis. Criteria for its use was based on safety considerations (Taras, 1968, Chanin, 1967 and Gruenfeld, 1977) and extraction efficiencies comparable to those obtained with petroleum ether and hexane, which were the previous standards. Both hexane and petroleum ether are flammable. However, several researchers (Wyer et al., 1981, Gruenfeld, 1977) have observed, that for petroleum type wastewaters, freon does not dissolve all the relevant components, particularly in heavier oils, such as No. 2 and No. 6 fuel oils. Likewise heavy, bituminous type oils, typically found in oilfield wastewaters are not as readily dissolved. Petroleum ether, for example, does not dissolve asphaltenes or bitumen (Wyer et al., 1981). More suitable solvents for effluents containing these types of oils are dichloromethane, trichloromethane, carbon tetrachloride, chloroform, benzene, toluene and xylene. Dichloromethane and carbon tetrachloride are currently being used in the heavy oil industry in Alberta (WTC, 1987). Similarly, in the monitoring of oilfield waste water generated from the production of oil from offshore facilities, hexane, carbon tetrachloride and dichloromethane have all been used (Wyer et al., 1981).

Of all the above solvents, freon 113 appears to be a reasonable compromise for most municipal and food-based effluents. Isopropyl ether, petroleum ether, and hexane have flammability problems; the aromatic solvents, benzene, toluene and xylene and the aromatic solvents carbon tetrachloride, and chloroform are carcinogenic (Patty, 1981). As shown in Table 9, the threshold limit value (1000 ppm) for freon 113 is significantly above the other solvents, meaning that it is less toxic and therefore safer to handle.

TABLE 9. THRESHOLD LIMIT VALUES FOR SOLVENTS USED FOR OIL AND GREASE ANALYSIS IN WATER

SOLVENT	CHEMICAL FORMULA	TLV ppm	RECOMMENDED BY	YEAR
Chloroform	CH_3Cl	0.5	ACGIH	1980
Dichloromethane	CH_2Cl_2	100	ACGIH	1980
Carbon tetrachloride	CCl_4	5	ACGIH	1980
Benzene	C_6H_6	10	NIOSH	1974
Trichlorotrifluoro -ethane (Freon 113)	$CClF_2-CCl_2F$	1000	ACGIH	1980

Notes:

TLV - The concentration of a substance in air that can be breathed for five consecutive eight-hour workdays (40 hour week) by most people without adverse effects.

ACGIH - American Conference of Governmental Industrial Hygienists

NIOSH - National Institute for Occupational Health and Safety

Adapted from Patty's Handbook of Industrial Hygiene, 1981.

The drawback of using freon is that it also dissolves sulfur compounds, certain organic dyes and chlorophyll (APHA, 1985) which may lead to a higher than actual value of the oil and grease.

The availability of freon and other halogenated solvents in the future may be limited because of the concerns about the environmental effects of chlorinated and flourinated hydrocarbons regarding the depletion of the ozone layer. Clearly, the trend towards limiting or eliminating production of such compounds will severely impact on the choice of solvent available of oil and grease analysis.

The selection of solvent for the oil and grease analysis has been based on the need for a fairly non-polar solvent that is safe for routine analytical work. However, as discussed above, no one solvent is appropriate to all the different types of wastewaters encountered and this has led to wide variations in the solvents used for the oil and grease analysis. Hence, comparison of oil and grease results from various sources becomes difficult especially when the solvent is not specified. Also, depending on the non-polar property of the solvent, water-soluble organics may also be extracted. Therefore, there is a need to standardize the use of solvents for oil and grease analysis in a logical fashion. For example, studies investigating several solvents as a function of wastewater type (e.g. produced water, meat-processing wastewater, sewage, etc.) should be conducted.

A clearer definition of oil and grease is also needed so that the solvents used would in fact, extract the specific organic compounds responsible for the undesirable properties of oil and grease. The present definition of oil and grease is purely operational, and is based on the extractability of organic material by the reference solvent. With the variability in solvents being used, this definition has no value. Hence, it is felt that specific organic compounds, representative of oil and grease, should be designated. Solvent choice could then be based on extractability of these organics. Considering the extensive information available on specific organics in wastewaters, a review of this information slanted towards defining oil and grease should be possible.

7.2.1.3 Emulsion formation. As discussed in Section 7.2.1, samples in which hard to break emulsions are formed are not suitable for analysis by the partition-gravimetric method. The soxhlet extraction method (see Section 7.2.3) is therefore, recommended by Standard Methods.

7.2.1.4 Evaporative losses. The partition-gravimetric method does not measure low boiling point fractions of oil and grease since the evaporation of solvent requires that the temperature of the water bath be 70°C. The distillation temperatures for light naphtha fractions (C_6-C_7) of petroleum ranges from 60 to 100 C while gasoline (C_5-C_{10} and cycloalkanes) distills at 40 - 250°C. Hence, some of the lighter fractions may be lost during evaporation of the solvent. Rotary evaporation using a vacuum and a water bath at 70°C is also used and is less susceptible to losses of volatiles.

7.2.1.5 Tedious operation. The extraction of the oil and grease components using a separatory funnel is a very tedious operation, particularly when many samples have to be processed. For large sample volumes, greater than 1 L, this method is not suitable. Hence, there is a need to develop an alternative method for large volume samples.

7.2.1.6 Detection limit. The partition-gravimetric method is appropriate for oil and grease concentrations greater than 10 mg/L (APHA, 1985). Some regulations specify that stormwater is considered free of oil and grease if the concentration is less than 5 mg/L (Alberta Environment, 1976, Environment Canada, 1975) recognizing that measurements are unreliable below this value.

Factors contributing to the detection limit are caused by high relative errors at low residue weights contributed by (i) the weight of the 125 mL flask compared to that of the residue after evaporation, (70 g versus 10 mg), (ii) the introduction of additional weight (dust, grease from hands, etc.) during handling of the container and (iii) increase in weight caused by adsorption of oxygen while cooling.

As mentioned previously, at least a 1 liter volume of sample should be used for concentrations greater than 25 mg/L. For lower expected concentrations of oil and grease, larger volumes should be used. However, because of the tedium of manual extractions, and difficulties in collecting and shipping large volumes of samples, the partition-concentrations of oil and grease is, therefore, unsuited for concentrations lower than 10-25 mg/L.

7.2.2 Partition-infrared method

In the partition-infrared method, Standard Method 503B, (APHA, 1985), the oil and grease components are first extracted into freon, using the separatory funnel extraction procedure as in the partition-gravimetric method (Section 7.1.1). However, quantification of the oil and grease is by infrared spectrophotometry. Similar standard procedures for the partition-infrared method are covered in ASTM 3921-87 (ASTM Methods, 1987), API method 733-58 (API, 1960) and various European procedures (CONCAWE, 1984).

7.2.2.1 Principles of infrared spectrophotometry. In infrared spectrophotometry, radiant energy having wavelengths in the range of 2.5 - 16 µm is absorbed by the organic molecules to supply the energy for interatomic movements (bond stretching, bond vibration and bond rotations). Each type of bond absorbs the infrared energy at a specific wavelength. The change in absorbance can be measured with the appropriate instrumentation and can be related to the concentration of specific organic groups (Flett, 1977).

In the determination of oil and grease in wastewaters, the absorbance of the infrared radiation is measured at wavelengths corresponding to the CH bond stretching energy which occurs at wave numbers of 2924 cm^{-1} and 2959 cm^{-1}. The former wavelength represents the CH_2 group while the latter represents the CH_3 group. (Wavenumber is the inverse of wavelength and is more commonly used). The aromatic CH bond also absorbs infrared radiation at 3030 cm^{-1}.

7.2.2.2 Procedure - Standard Methods, APHA, 1985. A standard consisting a reference oil is prepared by transferring about 1 mL (0.5 to 1.0 g) of the oil to a tared 100 mL volumetric flask. The flask is then weighed to determine the exact weight of oil. Solvent (Freon 113) is then added to the flask to dissolve the oil. If a suitable reference oil cannot be found, then a standard consisting of consisting of 37.5% iso-octane, 37.5% hexadecane and 25% benzene must be used. Serial dilutions of the stock standard solution are prepared to cover the range of interest. The solutions are then scanned over the range of 3200 cm^{-1} to 2700 cm^{-1}. The absorbances of the solutions measured at the peak maxima at 2930 cm^{-1} are then used to prepare a calibration curve. Near infrared silica cells are used. The path length of the cells can be varied. For a range of 4 to 40 mg/L, a cell path length of 1 cm is used. The solvent extracts containing the oil and grease from the sample are then scanned in the same manner as the standards and the appropriate concentrations of oil and grease determined.

The main advantage of the partition-infrared method is its low detection limit. The use of longer cell path lengths (up to 10 mm) allows as low as 0.4 mg/L to be detected. In addition, the ability to directly measure the oil and grease in the organic solvent eliminates evaporation with its inherent loss of oil and grease constituents. The partition-infrared method also lends itself to instrumentation, and therefore is suitable for analysing many samples. As will be discussed later in Section 8, portable field units based on infrared adsorption are available, as well as continuous on-line monitors.

Solvent extraction. Most of the limitations observed in extracting the oil and grease components apply in this method as well. However, several methods for extraction are used to overcome the tedium of extraction using a separatory funnel. These methods include use of a shaking machine for time periods ranging from 10 to 60 minutes, with 15 minutes being the most common, and magnetic stirring (CONCAWE, 1984). The various methods of solvent extraction however need to be evaluated to ensure that comparable extraction efficiencies of the oil and grease are obtained.

Calibration standard. The calibration standard should be representative of the oil and grease in the wastewater. The standard oil recommended by Standard Method is a reference crude oil generally used as feedstock for the process. However, there may be some variation with this crude oil and what eventually is found in the wastewater because of processing conditions. Alternatively, a standard consisting of a mixture of 37.5% isooctane, 37.5% hexadecane and 25% benzene as recommended by Standard Methods (APHA, 1985) can be used. Other methods use only 50% iso-octane and 50% cetane (ASTM, 1987) so that the use of the carcinogenic benzene is eliminated.

The absorbance value(s) at either one, two or all three wavenumbers are also used. Standard Methods and ASTM 3921-87 use the absorbance at wavenumber of 2930 cm^{-1}; the API method uses the absorbances at 2860 and 2930 cm^{-1}, while some of the European methods include the absorbance at 3030 cm^{-1}. In the original development of the partition-infrared method, Simard (1951) stated that use of all three wavenumbers would be more accurate than absorbance at a single wavelength. The suitability of the calibration standard (isooctane, cetane and benzene) was checked against a wide variety of waste oils from the refinery processes and final refinery products. The absorbance at a concentration of 16 ppm of these compounds was obtained and compared with that of the standard. Most of the waste oils (7 out of 8) corresponded to values ranging from 81 to 109% of the absorbance of the standard. Similar results were obtained for the refinery products with the range being 87 to 114% for 6 out of 8 products tested. However, No. 6 fuel oil was underestimated by the standard, having only 74% of the absorbance value of the standard. Over-estimation was also obtained with a heavy lubricating oil, the absorbance obtained being 126% that of the standard.

Figure 8 shows a typical infrared scan for a standard consisting of isooctane, octadecane and benzene. It can be seen that the absorbance contributed by the aromatic CH bond is relatively small. In general this tends to be obscured by the more predominant aliphatic CH bonds. Therefore, the presence of aromatic compounds will not be accurately detected.

Gruenfeld (1973) evaluated the accuracy and sensitivity of the infrared method, using various crude oils as the calibration standards. The purpose of the work was to

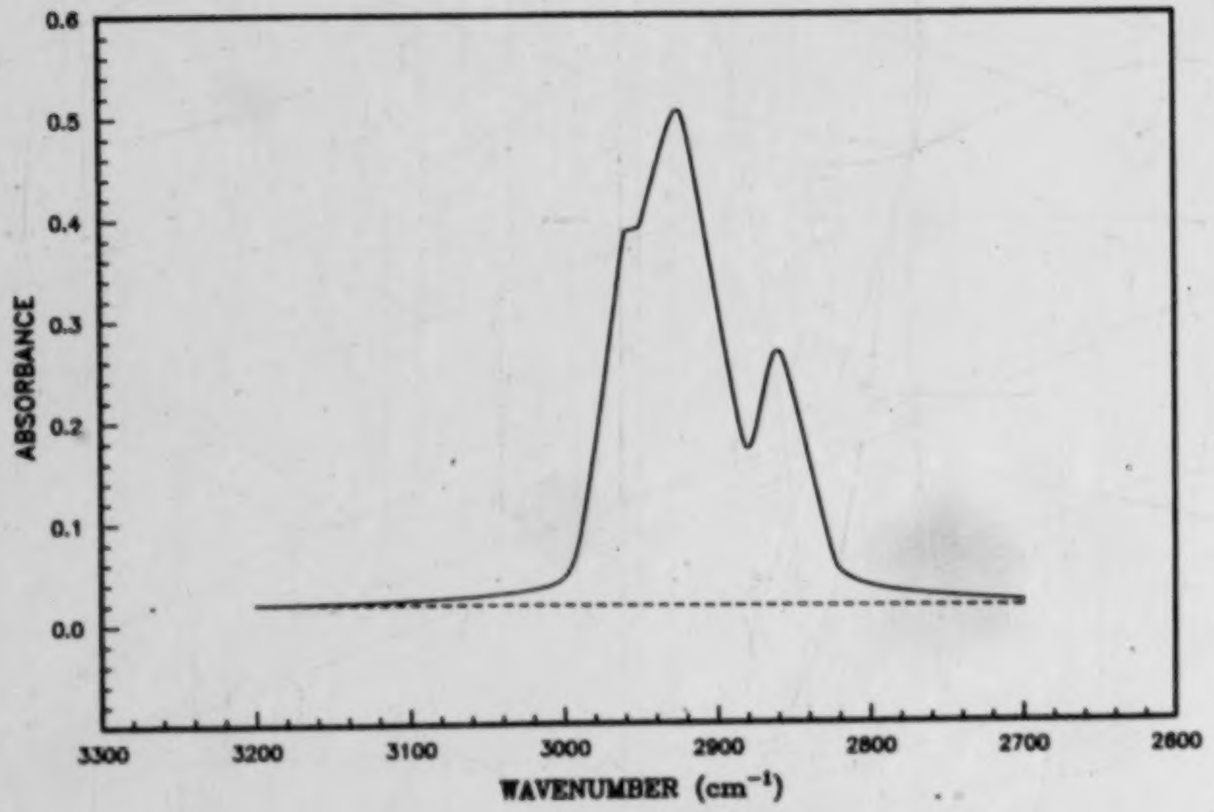


FIGURE 8: TYPICAL INFRARED SCAN FOR AN OIL AND GREASE REFERENCE STANDARD OF ISOOCTANE, OCTADECANE AND BENZENE

Adapted from ASTM, 1987.

determine whether single point determination of the oil concentration would be possible with the method. Single point determination relies on a linear relationship between absorbance and concentration. The concentration is determined from equation 2.

$$C_x = C_s \, (A_x/A_s) \text{ .... equation 2}$$

where: C_x = the unknown oil concentration of the sample extract

C_s = standard solution concentration

A_x, A_s = the absorbances of the sample extract and standard solution, respectively

The results of Gruenfeld's work indicated that linear relationships could be obtained for No. 2 fuel oil, South Louisiana crude oils at concentrations of 2 to 40 mg/L in water using Freon and 10 mm path length cells without ordinate scale expansion. For the concentration range of 0.5 to 3 mg/L of oil in water, either a 100 mm path cell length without scale expansion, or 10 mm path length cells with ordinate scale expansion of 5 could be used. For the 100 mm path length cells, absorbances should not exceed 0.7, since deviation from linearity would occur. For concentrations below 1 mg/L, deviations from linearity occurred for absorbance values above 0.7. Of all the oils tested, a heavy Bachaquero crude showed the most deviation from linearity. The deviation was most pronounced at low concentrations (0.1 to 0.7 mg/L) when a 100 mm path length cell at an ordinate scale expansion of 5 was used. Single point analysis at these levels was therefore not recommended for the heavy Bachaquero crude oil.

The choice of calibration standard must be carefully considered. The work by Simard and Gruenfeld suggests that for most oils, the method of using either a suitable reference oil or one based on a mixture of isooctane, cetane and benzene should be adequate. There is, however, some uncertainty when dealing with heavier oils, as reflected in both researchers' work. The increasing importance of such oils, as found in especially in the heavy oil and tar sands in Canada, would therefore, require some more research in the use of the method for monitoring waters from such sources.

Solvent choice. There are limitations with the solvent which can be used in the infrared method since the solvent must not absorb in the region of interest. Of the more common solvents, only freon (as specified by Standard Methods), carbon tetrachloride and possibly carbon disulphide can be used. Solvents such as dichloromethane which may be better for certain types of oils (as discussed in Section 7.2.1.2), have C-H bonds which absorb too strongly in the infrared region and would, therefore, overshadow the contribution of the oil extracted from the sample. A small amount of carbon tetrachloride in freon (2 mL carbon tetrachloride in 98 mL of freon) was used by Gruenfeld (1973) to assist in dissolving the heavier crudes found in petroleum type waters. However, the use of carbon tetrachloride should be limited because of its carcinogenic properties. Carbon disulfide is also not recommended because of its low TLV of 10 ppm (Weiss, 1986).

Other limitations. Another limitation of the partition-infrared method is cost. An investment of $6,000 to $21,000 for an infrared spectro-photometer is generally required (Nortech, pers. comm., 1986). Unless monitoring needs dictate that a large number of samples be analysed, then the cost of such equipment may not be justifiable. Most regulations specify the use of the partition-gravimetric method and hence, there is no incentive for the adoption of the partition-infrared method for discharge monitoring purposes. As will be discussed in Section 8, the partition-infrared method is useful for on-line process monitoring purposes.

7.2.3 Soxhlet extraction method

The soxhlet extraction method is used when heavy petroleum fractions and greases that do not easily dissolve in the organic solvent are present and also for samples where difficult-to-break emulsions are formed. The method is based on the Sanderson method as previously discussed in Section 7.1. A similar method is also incorporated in ASTM method 4281-B. The procedure as described by Standard Methods, Method 503C, is as follows: a 1 litre sample of acidified sample is filtered under vacuum through a bed of diatomaceous earth (Hyflo Super-Cel of equivalent) underlain by a muslin cloth disk and a filter paper (Whatman No. 40). The filter captures suspended oil and grease particles. When all the sample has passed through the filter bed, the filter paper is removed, and placed in a cellulose extraction thimble. The thimble is dried at 103°C for 30 minutes. After drying, the thimble is then placed in a soxhlet extraction device where the oil is dissolved in the solvent, Freon, for a period of 4 hours, using a soxhlet extraction rate of 20 cycles/hour. The solvent is then evaporated from the water bath. The residue and distilling flask is then cooled and weighed to yield the value for the oil and grease content.

The main limitations of the method are (i) losses during drying, (ii) control of extraction cycles and (iii) detection limits.

7.2.3.1 **Evaporative losses.** Losses caused by volatilization of the oil and greases during drying of the cellulose extraction thimble may occur. An indication of the extent of these losses has already been presented in Section 7.2.1.4.

7.2.3.2 **Solvent extraction.** The different solubilities of greases in the wastewater dictate that the rate and time of extraction in the Soxhlet extraction unit should be suitably adjusted. It is difficult to control the exact number of cycles.

7.2.3.3 **Applicable range of concentrations.** The method is not suitable for samples having considerable free oil since the free oil will retard effective filtration of the sample, and result in excessive time required for filtration. The oil and grease concentration in the sample should range from 20 to 200 mg/L (ASTM, 1987).

7.2.4 Methods for separation of oil and grease from different origins

The current standard method for distinguishing between oil and grease from the different sources is based on the adsorption of polar oils from the solvent extract. The adsorbents used have a high affinity for polar organics as is typical of animal greases and vegetable oils. The petroleum based oil and grease therefore remains in the solvent extract. The adsorbent also adsorbs complex aromatic hydrocarbons and chlorine-sulphur-nitrogen hydrocarbon derivatives, which would be dissolved in Freon. Therefore, this procedure is also suitable for removing these interferences.

The procedure allowed by Standard Methods APHA, 1985 consists of drying 60 to 200 mesh silica gel adsorbent at 110°C for 24 hours. The solvent extract from any of the methods for determining total oil and grease is then mixed with 3.0 g of the silica gel in a closed container using a magnetic stirrer. Quantification of the unadsorbed portion, i.e. hydrocarbons, can then be directly accomplished using infrared spectrophotometry or by gravimetry (after filtering the solution and washing the silica gel with solvent). In work cited by Standard Methods, the average recovery obtained for hydrocarbon determinations on 10 synthetic solvent extracts was 97.2%. Complete adsorption of extracts of vegetable and animal type oil and grease (Wesson oil, olive oil, Crisco and butter) was obtained, as evidenced by zero detection using infrared analysis.

The ASTM method (D 3921) specifies the use of 2% deactivated silica gel. This method requires drying a fixed amount of silica gel (100 to 200 mesh) washing and removal of solvent. The silica gel is then dried, initially at 100°C to drive off the solvent and then at 150°C for 2 hours. After drying and cooling in a dry atmosphere to room temperature, water equal to 2% of the weight of the silica gel is added. After shaking, the container is left to stand for several hours to reach equilibrium.

Other adsorbents proposed for removing the polar organic interferences are molecular sieves (Uchiyama, 1978) and Florisil (McCrum and Whittle, 1982). Molecular sieves are aluminosilicates which have been heated to remove the water of hydration. They possess high porosity and pores of uniform size in the molecular size range (4 to 5 angstroms) and have a high affinity for unsaturated and polar molecules (Perry and Chilton, 1973). Uchiyama used a molecular sieve MS5A and heated it to 400 to 500°C for 3 hours to remove any adsorbed water. The oils used were mineral oils (heavy oil, machine oil, engine oil), animal oil (beef tallow, lard, whale oil) and vegetable oil (rapeseed oil, soybean oil, cottonseed oil, olive oil). Each oil was dissolved in carbon tetrachloride to a concentration of 1 g per 10 mL of solvent. Three g of MS5A were added to the solution and shaken occasionally.

The results indicated that the mineral oils were either not adsorbed or adsorbed at a very slow rate by the molecular sieve. The animal and vegetable oils were adsorbed within 1 hour. The method of determining the amount of mineral oil that was not adsorbed was based on a calibration standard of oleic acid, which had been found to average the infrared absorbance behavior of the mineral oils tested. Uchiyama concluded that no hydrocarbons were present in actual waters tested.

Florisil is a magnesia-silica gel adsorbent. The work by McCrum and Whittle, 1982, involved the extraction of dispersions of gas oil, petrol, white spirit and lubricating oil with carbon tetrachloride and Freon in separate tests. Materials tested for interference were soya bean oil, herring oil, tallow, phenol and anachidic alcohol. The extracts were passed through a 3 cm deep column of Florisil which had been prepared by heating at 400°C in a silica basin for 2 hours. After cooling, a weighed amount of Florisil was placed in a bottle and 6% by mass of water was added and mixed for 1 hour to provide a desirable level of adsorbent activity.

All the materials tested for interference were removed by the Florisil. It should however be noted that Gruenfeld (1977) citing Longbottom, 1975, indicated that Florisil was less effective than silica gel for removing the polar oil compounds.

7.3 Comparison Between the Standard Methods for Oil and Grease Analysis

In this section, the three standard methods for oil and grease analysis are compared. There are three considerations in evaluating or comparing methods: accuracy, bias and precision. Taylor (1988) defines these terms as follows:

- Accuracy is the degree of agreement of the measured value with the expected value of concern.
- Bias is caused by systematic errors inherent in a method or caused by some artifact of the measurement system. Examples of the former type of errors are

extraction inefficiencies or temperature variation; examples of the latter type are calibration errors, contamination and mechanical losses. Bias may be positive or negative. Since several sources of bias exist concurrently, only net bias can be determined. Precision is the degree of mutual agreement between independent measurements obtained from repeated applications of the same process at given conditions.

The most extensive precision and bias data for oil and grease determination in water are presented in the ASTM Methods for oil and grease determination in water (ASTM, 1987). The procedure used to obtain this data involved independent analyses by different laboratories. For the partition-gravimetric procedure, 9 operators from 9 laboratories determined 4 concentration levels of oil and grease in reagent water over 3 days. For the soxhlet extraction method, 6 operators from 4 laboratories determined 3 concentration levels over 3 days. For the partition-infrared method, a group of 18 samples representing 6 concentration levels of oil and grease in triplicate was analyzed by one operator in each of 18 different laboratories.

The precision and bias data for all three methods are shown in Table 10. Figures 9 and 10 show precision and bias data for the partition-gravimetric and the Soxhlet extraction methods respectively.

As shown in Table 10, for the partition-gravimetric method, the relative bias is highest at 19.4% at the 4.4 mg/L level, indicating a significant difference between the spike

TABLE 10. PRECISION AND ACCURACY OF METHODS FOR OIL AND GREASE ANALYSIS IN WATER

Method of Analysis	Spike Conc. mg/L	Conc. Obtained mg/L	% Recovery	% Bias	Significant
Partition-Gravimetric	4.4	5.3	120.0	19.4	yes
	13.1	13.9	106.1	6.0	yes
	21.9	22.3	101.8	1.8	no
	65.7	62.4	95.0	-5.0	yes
Soxhlet Extraction	20.7	18.8	90.8	- 9.0	yes
	73.6	64.4	87.5	-12.6	yes
	151.0	135.0	89.4	-10.6	yes
Partition-Infrared	16.4			2.4	
"	(0.6- 66)	$P_t^1 = 0.167x + 0.333$ $P_{o2} = 0.122x + 0.148$ $P_t = 0.160x + 0.329$			
hydrocarbon[3]		$P_t = 0.141x + 0.048$			

Notes:
[1] - overall operator precision
[2] - single operator precision
x - concentration determined, mg/L
[3] - hydrocarbon-silica gel method

Adapted from ASTM, 1987.

concentration and the determined concentration. The bias may be positive or negative, indicating that the method will overestimate at the lower levels (less than 13.1 mg/L) and underestimate at higher levels (65.7 mg/L).

For the soxhlet extraction method, the relative bias is always negative indicating the method will tend to underestimate the true value. The bias for the partitition-infrared method was +2.4% at the 16.4 mg/L level, which is similar for the partition-gravimetric method at this concentration level (by interpolation).

Figures 9 and 10 indicate that the precision is curvilinear with concentration for the partition-gravimetric and the soxhlet extraction methods. The relationship of precision with concentration for the partition-infrared method is linear as indicated by the equations in Table 10. Two types of precision are presented for the partition-infrared method, overall precision, and single operator precision (S_t and S_o respectively). Overall precision reflects differences between several laboratories, while single operator precision refers to the experimental variations of a single operator. It is important to note that the relative deviation from the mean is higher at the low concentrations than at higher concentrations for both types of precision. From Figure 9, for a single operator and the partition-gravimetric method, the relative deviation at 4.4 mg/L is 31.8% while at 65.7 mg/L concentration, the relative deviation is only 3.3%.

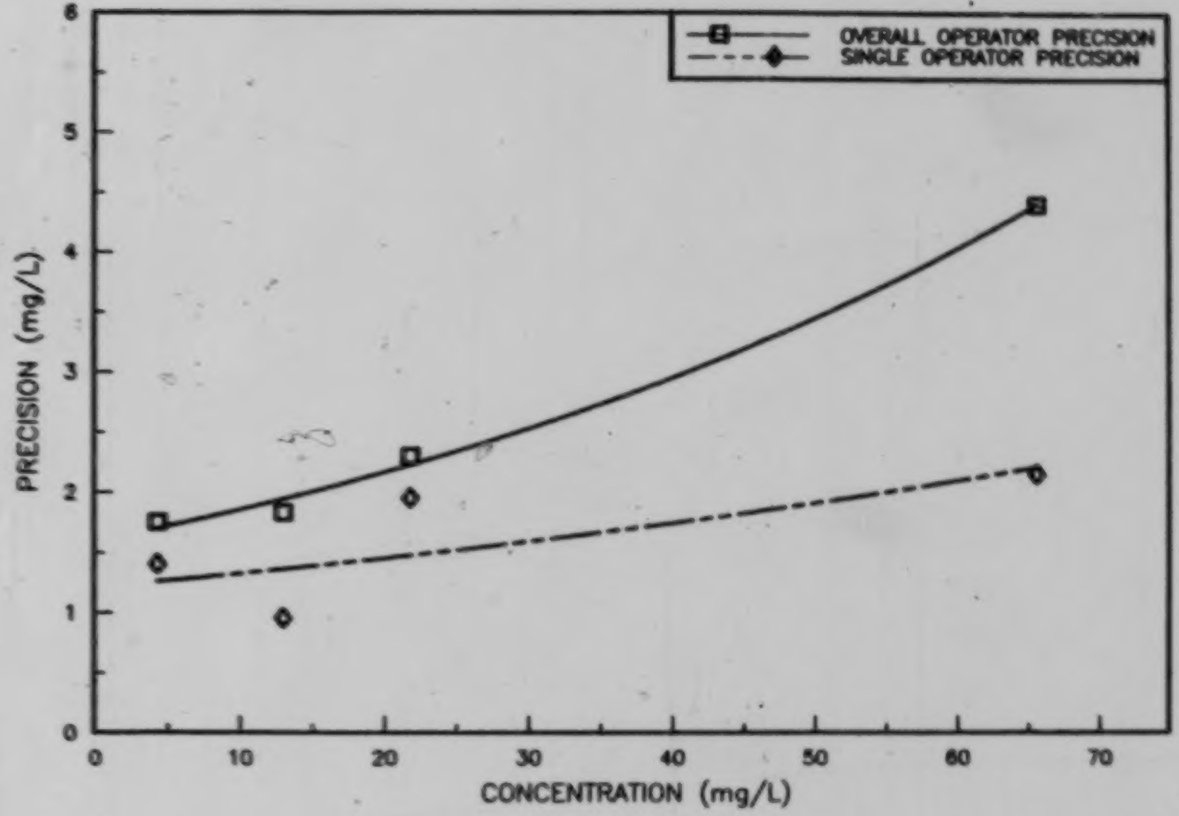


FIGURE 9: PRECISION vs CONCENTRATION FOR PARTITION–GRAVIMETRIC METHOD FOR DETERMINATION OF OIL AND GREASE IN WATER

Adapted from ASTM, 1987.

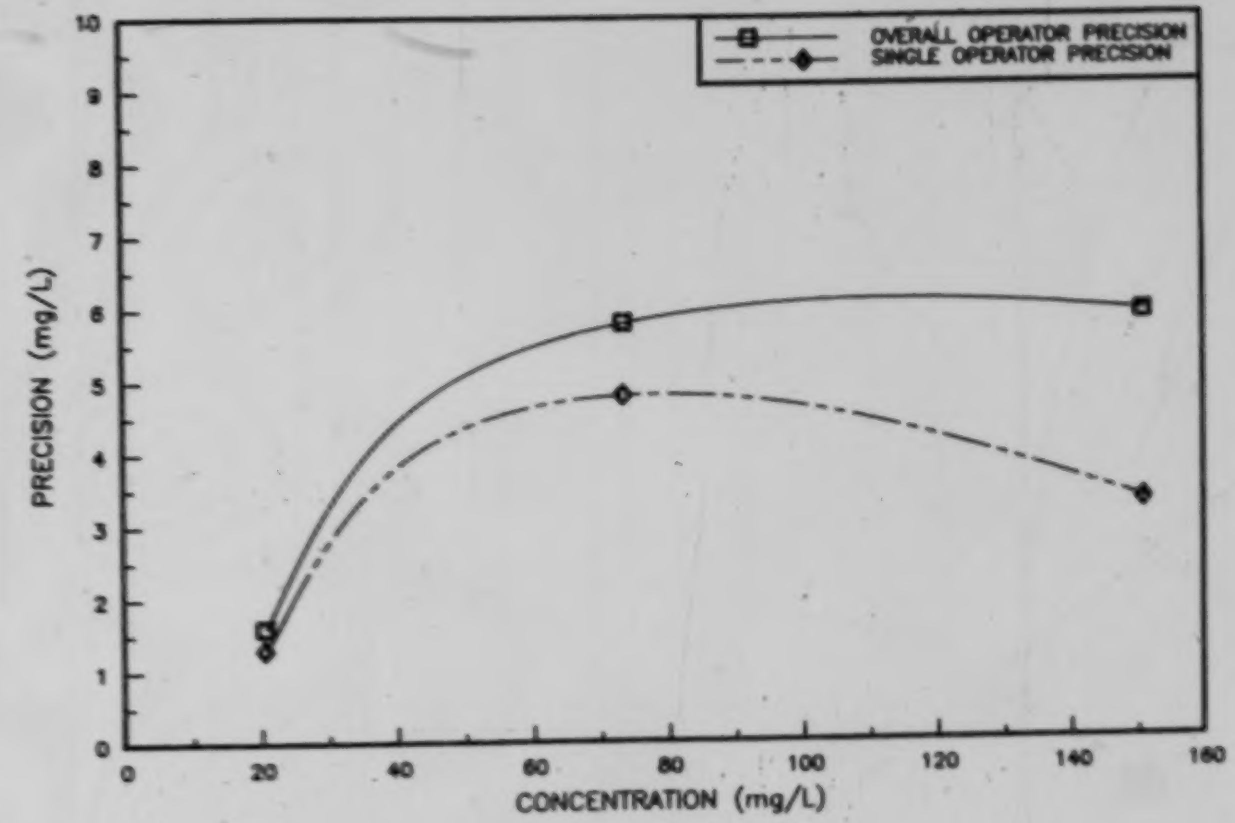


FIGURE 10: PRECISION vs CONCENTRATION DATA FOR SOXHLET EXTRACTION METHOD FOR DETERMINATION OF OIL AND GREASE IN WATER

Adapted from ASTM, 1987.

By comparison, the partition-infrared method has a much lower relative deviation of 15.2% at the 4.4 mg/L level for a single operator precision. The relative deviation for the soxhlet extraction method is less than 6.7% for single operator precision for all concentrations measured, as shown in Figure 10. It should be noted that the limited data presented by ASTM do not allow any more substantive interpretation of the relative reliabilities of these methods.

Data on actual wastewater samples produce widely varying results. Rewick et al.(1981) compared the partition-infrared and partition-gravimetric method for oilfield produced waters from two offshore platforms. These results are shown in Table 11. In both cases the partition-infrared method produced higher oil and grease values. For the Dillon platform, the average value obtained by partition-infrared analysis was more than double that obtained by partition-gravimetric analysis. For the Shell sample, the oil and grease value measured by the partition-infrared method was 35% higher.

The lower values obtained by the partition-gravimetric method compared to the infrared method are usually attributed to the losses caused by volatilization of lighter fractions when the solvent is evaporated. However, since both methods of quantification are distinctly different, the absolute values of oil and grease cannot be compared.

Comparison of the precision (reproducibility) of both methods (see Table 11) indicated that the partition-gravimetric method produced a greater standard deviation for samples than the

TABLE 11. **COMPARISON OF INFRARED AND PARTITION-GRAVIMETRIC METHODS FOR OIL AND GREASE ANALYSIS IN OILFIELD PRODUCED WATERS**

SAMPLE	OIL AND GREASE CONCENTRATION, mg/L	
	INFRARED	PARTITION-GRAVIMETRIC
Dillon No. 1	54.6	17.5
No. 2	48.1	18.5
No. 3	36.3	19.3
No. 4	45.9	23.6
No. 5	56.6	5.5
No. 6	45.7	19.5
Average	47.9	17.3
Std. Deviation	7.3	6.2
% Std. Deviation	15.2	35.8
Shell No. 1	34.2	20.2
No. 2	40.7	35.0
No. 3	35.2	31.6
No. 4	36.6	37.0
No. 5	38.1	23.9
No. 6	44.1	21.7
Average	38.2	28.2
Std. Deviation	3.7	7.2
% Std. Deviation	9.7	25.5

Adapted from Rewick, 1981.

partition-infrared. For the Dillon sample, the percent standard deviation for the partition-gravimetric method was 35.8 while that for the Shell sample was 25.5. Comparative percent standard deviation for the partition-infrared method were 15.2 and 9.7 respectively. Therefore, there is less variability in the partition-infrared method. This is also confirmed in the results of the precision study conducted by the ASTM as previously discussed.

Somewhat conflicting results are discussed by Wyer et al.(1977). As shown in Table 12, for a California coastal sample of an oilfield wastewater from an oil removal system, the partition-gravimetric method yielded 8.2 to 28.5% higher values than the partition-infrared method. By contrast, for the Texas Coastal samples, the infrared method values were slightly higher than those obtained using the partition-gravimetric method except for one value in the highest concentration range measured (in the 200 mg/L range). Table 12 also shows data when petroleum ether solvent is used instead of Freon. The difference between solvents is dramatic. Petroleum ether in two cases, extracted less than one-third that of Freon.

Data comparing oil and grease concentrations obtained by different laboratories using the same method was substantially different. Insufficient information was presented in this paper to identify the causes for the discrepancy, although the author felt that the analytical technique of the laboratory was most likely the cause. However, these type of data reflect the wide

TABLE 12. **OIL AND GREASE VALUES IN TREATED OILFIELD WASTEWATERS**

SAMPLE LOCATION	CONCENTRATION OF OIL AND GREASE, mg/L				
	LABORATORY 1			LABORATORY 2	
	Freon/ Gravimetric Method	Freon/ Infrared Method	Petroleum Ether/ Gravimetric Method	Petroleum Ether/ Gravimetric Method	Freon/ Gravimetric Method
California Coastal					
C-1	22.3	16.0	5.0	3.1	5.0
C-2	42.2	39.0	27.0	3.6	145.0
C-3	46.1	35.0	7.0	11.2	10.0
Texas-Coastal					
T-1	126.0	154.0			
T-2	242.0	197.0			
T-3	52.0	62.0			
T-4	46.0	51.0			

Note: Designations C-1, C-2, C-3, T-1, T-2, T-3, T-4 refer to different oil platforms

Adapted from Wyer et al., 1977.

variability that occurs in the sampling and analysis of oil and grease.

7.4 Other Methods for Determination of Oil and Grease in Water

7.4.1 Continuous extraction method

A continuous liquid-liquid extraction procedure (using petroleum ether) for handling hard-to-break emulsions was developed by Hrudey (1981). The method was tested on synthetic dispersions of oleic acid in water at concentrations of 5 to 100 mg/L, spiked secondary effluent samples, and samples to which humic acid had been added. Comparative tests between the partition-gravimetric method and the soxhlet extraction method (Standard Methods, APHA, 1985) were also conducted. The effect of increasing the extraction time for the soxhlet extraction method from 4 to 16 hours was also investigated.

The percentage recoveries obtained for a 100 mg/L oleic acid dispersion was 97.0% for the continuous extraction method, compared to 82.5 and 86.1% for the standard partition-gravimetric and soxhlet extraction methods.

The standard errors were 1.4%, 1.9% and 1.8% for the partition-gravimetric, soxhlet extraction and continuous extraction methods respectively.

Results of the continuous extraction method for concentration ranging from 5 to 100 mg/L indicated that the continuous extraction method was significantly better for the low concentration range (5 to 25 mg/L) for spiked sewage samples that the partition-gravimetric method.

Addition of 2 mg/L humic acid (which was felt to be a reason for the variability in results of both methods because of its emulsion formation properties) resulted in poorer recovery of oleic acid using the separatory funnel method and a greater standard error (1.4% versus 0.6% for the liquid-liquid extraction procedure). The recovery using the continuous liquid-liquid extraction method was 86.5% compared to 77.4% for the partition-gravimetric method.

7.4.2 Spectrophotometric methods

These methods rely on the supply of energy in various forms, to excite the component electrons of the hydrocarbon molecules in the oil. These electrons, in turn, can either (i) absorb the energy (absorbance), resulting in a reduction in the intensity of the original energy supplied or (ii) emit energy which can be detected by photometers (fluorescence). The spectrophotometric methods differ in the wavelength of the energy supplied, the mode of transmission of the energy and the way in which the energy output is detected. The infrared method has been previously discussed in Section 7.2.

7.4.2.1 UV-visible light adsorption. Thayer, 1985, developed a method based on spectophotometric detection in the ultraviolet-visible (uv-vis) region. It offers potential advantages over the infrared mode of adsorption method since the requirement for a solvent with no CH bonds is eliminated. The method is based on the color intensity of the oil components in petroleum-based effluents after solvent extraction. It was found that the absorbance of the coloured solvent extracts containing the oil fraction in the wastewater followed Beer's Law, and that appropriate standards could be prepared from the raw crude oil.

This method of quantitation is used extensively in the heavy oil industry for determining oil and grease in produced water (Hydromation, 1985, WTC, 1988). The applications include monitoring the efficiency of induced gas flotation and filtration processes. The wavelength at which the oil concentration ranges from 360-400 nm.

7.4.2.2 Vapor phase ultraviolet adsorption. In a vapor phase ultraviolet adsorption method developed by Thompson and Wagstaff, 1979, a small sample (0.1 to 10 µL) of a solvent extract containing the oil and grease was placed in a small graphite tube which is slowly heated. The adsorption of the solvent extract was monitored during heating to produce a trace of absorbance versus time. The heating medium used was a Varian electrothermal atomiser and the sample was heated from ambient temperature to 900°C. Oils tested ranged from mineral related substances such as lubricating oils, gear oils, cutting oils, and vegetable based oils (cooking oils, margarine, butter, beef dripping and linseed oil). The wavelength at which the absorbance was measured was 190 nm. The solvent used for extracting the organics from water was either hexane or chloroform.

The method was designed to allow fingerprinting of organics in water. Actual river samples containing suspected spill components (Triton X-100 detergent, and pentachlorophenol) were tested. The resulting traces were then compared with traces of the pure compounds. Although the authors presented both traces and felt that the spill components could be positively identified, the results showed that the concentrations were too low to allow an appreciable absorbance (less than 0.025) from which actual concentrations could be determined. Therefore, the method is probably limited to fingerprinting only.

7.4.2.3 Fluorescence. In fluorescence, energy is emitted as electrons in the molecules return to ground energy level, after being excited by the incident radiant energy. In petroleum oils, fluorescence is caused by the presence of aromatic molecules. Typical crude oils contain from 10 to 30 percent aromatics, of varying molecular size and configuration. Therefore, the emission wavelength for a petroleum oil would be a result of the combined emission characteristics of its constituent aromatic compounds.

Maher (1983) conducted experiments using fluorescence for routine monitoring of petroleum hydrocarbons in estuarine water and seawater. Dispersions of crude and refined oils in water were extracted with dichloromethane after adjusting the dispersion to pH 4-5. The dichloromethane was then evaporated and the residue dissolved in hexane. The hexane solutions were then excited at 300 nm, the emission scanned from 310 to 500 nm and the fluorescence emission intensity of the main peaks measured and reported as equivalents of m-Terphenyl (emission wavelength - 330 nm) and chrysene (emission wavelength - 380 nm). m-Terphenyl and chrysene were selected as reference standards, based on examination of emission spectra of several crude oils and refined oil products. These spectra showed that the oils could be classified into two groups, one group containing two and three ringed aromatic compounds with a fluorescence emission intensity of 330 nm and another group containing three or more aromatic rings with a fluorescence emission maximum at approximately 380 nm. Since m-Terphenyl and chrysene exhibit wavelengths of maximum emission at 330 and 380 nm respectively, they were selected as the reference standards.

Interferences by humic acids, chlorophyll pigments and detergents were found to be negligible (less than 2% change in emission intensity). Recoveries of one litre samples of seawater, spiked with 1 µg of various crude oils, and lubricating oils were reported to be greater than 95%. The relative standard deviation was less than 2%. Actual samples taken from potential sources of petroleum hydrocarbon inputs (oil refinery, boat marina, sewer outfall, stormwater drain, river and seawater) were analysed at both emission wavelengths. The lowest concentration measured was for a river water sample at 176 and 114 ng/L as m-Terphenyl and chrysene respectively. The concentrations of oil and grease in waters sampled at an oil refinery and boat marina were of the order of 1000 to 2000 ng/L.

Improvements to the fluorescence method to allow detection of low concentrations of hydrocarbons in aqueous medium have been proposed by John et al, 1982. The main problems experienced with fluorescence techniques were non-linearity and poor reproducibility of the observed emission intensity obtained with concentration of dispersed crude oils in water. They modified the conventional fluorescence cell so that rapid adsorption of the sample onto the quartz optical surface was eliminated. From the paper, it is not clear as to how a clean optical surface was maintained. However, results did indicate linearity of fluorescence intensity with concentration for three crude oil samples tested at concentrations ranging from 2 to 10 µg/L.

7.4.2.4 Flame emission spectroscopy. In a flame emission spectroscopy developed by Pragar and Stainken, 1981, the energy for excitation of the electrons in the hydrocarbon was provided by a hydrogen flame. The emission produced on combustion of the oil in water was then used to determine the concentration of the oil in water. The emission wavelength used was431 nm.

Tests were conducted by preparing dispersions of pure compounds (benzene, heptane) and fuel oils (No. 4, No. 6) in saline water. The individual dispersions were then fed into the hydrogen flame as an aerosol, which was produced using an ultrasonic nebullizer. Several difficulties were encountered with the technique. The most important one was interference by the presence of sodium chloride and other metal ions. Steam distillation (steam temperature was 538°C) to separate the organic fraction from the interfering metal ions was used to overcome this problem. Control of the flame temperature by adjusting the amount of nitrogen used was also needed to prevent background interference.

The method was able to detect down to 1 ppm of benzene in water, and 10 ppm of No. 2 and No. 4 fuel oil in water.

7.4.3 Light scattering and turbidity

In light scattering methods, a ray of light is directed onto the oil droplets and the change in intensity of the incident light and the light scattered or reflected after impingement on the oil droplets is measured. In turbidity measurements, the decrease in the light intensity transmitted through the sample is measured. In measurements using light scattering and turbidity, it is important to have a constant particle size diameter of the oil droplets, and hence some homogenization of the sample is needed prior to measuring. The method is subject to interferences by other particles such as rust and silt, both of which may be present in typical oily water samples. The method has been extensively applied in oil in water monitors as discussed later in Section 8.

In a method proposed by Kawahara and Fiutem, 1983, a sample of oily water was passed over the surface of an optical fibre which was inserted in a coiled, stainless steel housing. The optical fibre was coated with an organophilic compound which adsorbed the hydrocarbons in the wastewater. A change in the refractive index of the incident radiation (wavelength=632 nm) caused by the adsorbed oil was then measured. The variation in the output signal was found to be related to the concentration of the hydrocarbon in the water. A low power laser provided the incident radiation.

The optic fibre used was fused silica because of its low refractive index, compared to other materials (plastic, glass and sapphire). Relative to the refractive index of many organic compounds, the index of refraction for the fused silica is high. Hence, light entering the fiber is retained within the fiber by total internal reflection, and is transmitted with relatively low attenuation to the opposite end of the fibre, as shown in Figure 11.

Organophilic coatings tested were octadecyltrichlorosilane, diphenyldichlorosilane, n-decyltrichlorosilane and tri-n-octylamine. Octadecyltrichlorosilane produced the best overall results, based on its ability to detect the lowest concentration of oil in water. Pure hydrocarbons tested were heptadecylbenzene, dodecylbenzene, n-hexyl benzene, tert-butylbenzene, o-xylene, m-xylene, p-xylene, chlorobenzene, ethylbenzene, chlorobenzene, 2,6-dimethylstyrene, cyclohexylbenzene, tetralin (1,2,3,4-Tetrahydronaphthalene), bromobenzene, 3,3-dimethylbiphenyl, phenanthrene, 1-methylnaphthalene, 1-phenylnaphthalene. Diesel fuel and crude oil were also tested. Hydrocarbon concentrations ranged from 1 mg/L to 1000 mg/L. Linear responses of the rate of light transmission loss (expressed as decibels/s) with concentration (above a certain threshold value) were obtained. The threshold value varied with each compound. This value appeared to be related to the solubility of the compound based on the results presented for n-hexylbenzene, p-xylene, tetralin, diesel oil and crude oil.

The system was able to detect diesel oil in water at 17 mg/L and crude oil at 3 mg/L. Corresponding detection limits

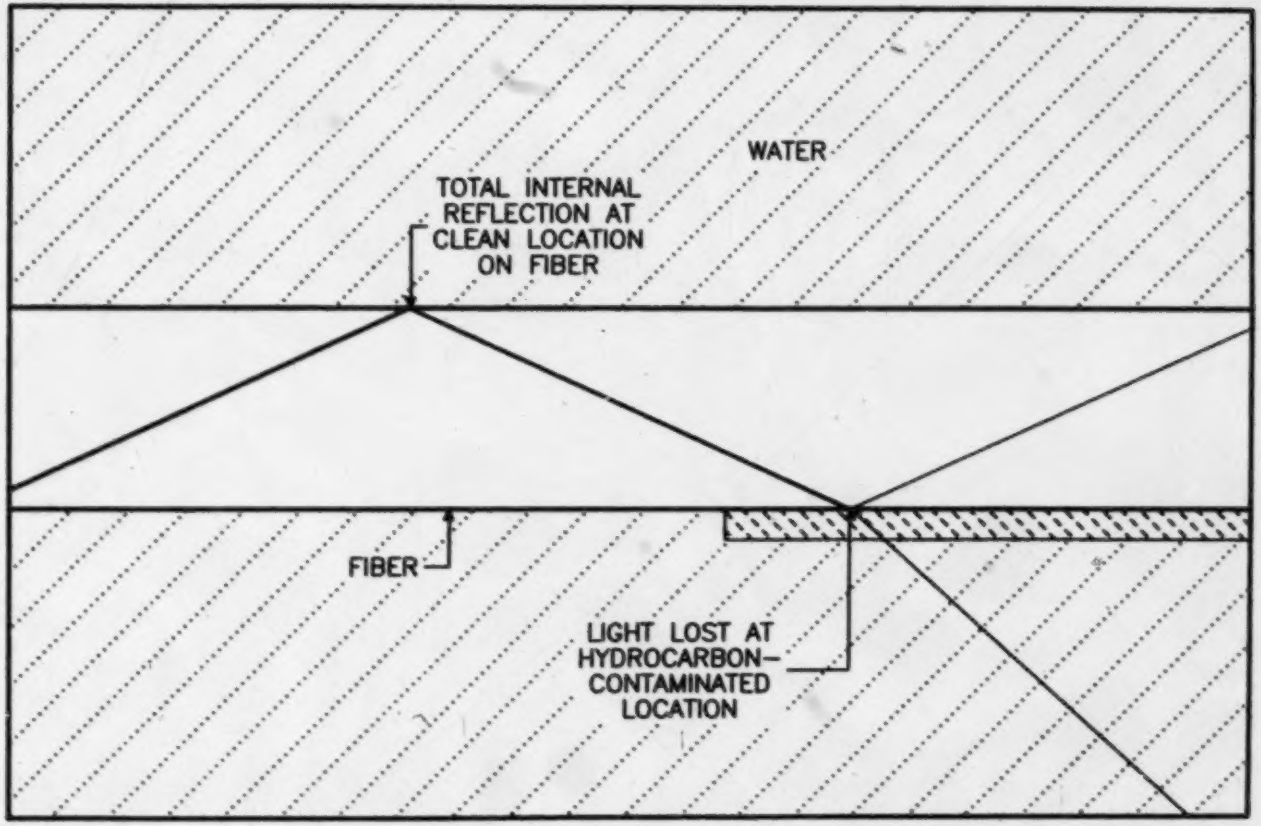

WATER
TOTAL INTERNAL REFLECTION AT CLEAN LOCATION ON FIBER
FIBER
LIGHT LOST AT HYDROCARBON—CONTAMINATED LOCATION

FIGURE 11: PRINCIPAL OF LIGHT TRANSMISSION METHOD FOR DETERMINATION OF OIL AND GREASE

Adapted from Kawahara and Fiutem, 1983.

for n-hexylbenzene, tetralin and p-xylene were 2, 30 and 400 mg/L.

The system required sophisticated instrumentation, and has not been field tested. Optimization of methods for coating the optical fibres and testing of more appropriate coatings was felt to be needed (e.g. a combination of octyldecyltrichlorosilane and diphenyldichlorosilane was felt to be more appropriate for crude oils) to check the method's suitability for more realistic applications.

7.4.4 Multiphase dye transfer

A method involving the use of a dye which would solubilize only oil was developed by Ricci and Kelly, 1977. This method consisted of filtering an aqueous sample through a Reeves-Angel boro-silicate glass filter (47 mm diameter), pressing the filter against a dye pad impregnated with Oil Blue B dye and measuring the dyed sample using a direct photometric method to determine the quantity of oil particles present in the water sample. The oil was transferred into the dye by compressing the filter and the dye impregnated pad between two stainless steel plates at a pressure of 770 KPa for three minutes. The dye selectively transferred to the oil particulates on the filter, causing a blue coloration. The intensity of the color was found to be proportional to the amount of oil entrained on the filter. The intensity of the blue color was then measured using a reflectance meter.

Reflectance values for tests conducted with oil in water dispersions in the concentration range of 0 to 30 mg/L showed standard deviations of less than 2% for all concentrations. A field unit was built, and consisted of all the filtration assembly including vacuum pump, the dye transfer assembly (compression of the filter is by adjustment of a calibrated spring) and a Photovolt Corp Model 679 photometer. Testing of the field unit for shipboard monitoring indicated that the method required further evaluation to reduce the variations in output with oil type, to optimize the reflectance wavelength for the Oil Blue B dye, and to compensate for the presence of interferences such as particulates and filter discoloration.

This method merits application in the area of pure component tests where it is desirable to know the content of the dispersed oil. In actual field situations where samples are apt to be colored and contain surfactants, excessive interference will probably limit its application.

7.5 Summary of Methods

The most promising alternatives are the liquid-liquid extraction method (Hrudey, 1981), the UV-visible light adsorption method (Thayer, 1985) and light scattering methods (Kawahara and Fiutem, 1983). The liquid-liquid extraction method has the advantage of being able to handle emulsifying type samples, and the ability to handle lower concentrations than for the standard Soxhlet extraction method. Equipment requirements are minimal and readily available. The main limitation is the limited sample size which would restrict detection by gravimetry into the same range as the partition-gravimetric procedure (i.e. <25 mg/L).

The UV-visible light adsorption method also requires extraction into an organic solvent. Unlike the infrared method of detection, the choice of solvent type is not as restrictive. A spectrophotometer is required. Like all spectrophotometric methods, an appropriate calibration standard is required, and checks on the standard be conducted to ensure the calibration standard is valid.

Light scattering methods also provide some degree of simplicity. However, these methods are subject to interferences such as suspended particulate materials. Despite this, these methods are mostly applied in on-line continuous monitoring rather than in batch sampling and analysis. Fluorescence has also been used in oil spills identification applications and in on-line continuous monitors. Like all spectrophotometric methods, it relies on an appropriate calibration standard.

The multiphase dye transfer procedure is limited in application as it requires specialized equipment and is subject to interferences by particulate and other colored matter in the water. The vapor phase adsorption technique also seems complicated for routine analysis.

None of the above methods specifically address the distinction between dissolved and dispersed oil. The dispersed oil probably is best measured by light scattering methods such as turbidity. Some sample preparation could theoretically be incorporated in these methods for capturing suspended oil, however, this has not been the case to date.

8 OIL IN WATER MONITORS

The purpose of oil in water monitors is to allow quick analysis of the oil in the wastewater. Rapid measurement of the oil parameter allows control of oil removal processes so that upset conditions could be readily resolved, thereby minimizing excessive discharges of the contaminant, or upsets to downstream operations.

Parker and Pitt (1987) reviewed oil in water monitoring applications, and the commercially available oil in water monitors. Table 13 lists oil in water monitoring applications and their problem areas for on-line monitoring. The range of concentrations range from 0 to 1000 ppm, depending on the application. Boiler condensate require levels down to 0 to 2 ppm with an accuracy of ±0.1 ppm. More commonly, levels of up to 30 ppm are required with an accuracy of ± 5 to 10 ppm (Pitt, 1987).

Continuous, on-line oil in water monitors are most extensively applied in the monitoring of oily bilge and ballast water from ships and oil tankers. Ballast water refers to the water used to replace the volume of oil in storage tanker vessels after the oil is unloaded. This water is, in turn, discharged when a new cargo of oil is loaded at the filling terminal. The contaminated ballast water is treated prior to discharge using oil removal systems. Oily bilge water is water that is washed off the floors of machinery areas, such as the engine room, where oil (primarily lubricating type oil) accumulates. This water

TABLE 13. OIL IN WATER MONITORING APPLICATIONS

APPLICATION	CONC. RANGE mg/L	COMMENTS/PROBLEM AREAS
Dirty ballast	0 - 1000 ± 20% or ±10 mg/L (whichever is greatest)	Used for discharge outside coastal limits. Must measure all types of oils, including crude oils and light oils. Must consider interference by background solids of sand and rust, and clogging with certain oils.
Clean ballast	0 - 20 ± 10 mg/L	Discharge inside coastal limits. Must consider interferences by background solids of sand and rust.
Bilge recorder	0 - 100	Used for bilge discharge outside coastal waters. Must consider interferences by detergents, additives, solids.
Bilge alarm	0 - 15 ± 5 mg/L	Used for alarms on discharge outside coastal limits.
Oil rigs	0 - 70	Used for monitoring oil/water separation processes. Must consider problems caused by solids, clogging by waxy precipitates, presence of gases. Hazardous space requirements for safety are often specified.
Refinery	0 - 30 ± 5 mg/L	Must consider background interferences by solids, dissolved hydrocarbons and salts.
Boiler condensate	0 - 2 ± 0.1 mg/L	High accuracies required with low instrument drift.
General water	0 - 50	Interferences by background solids and dissolved compounds.

Adapted from Parker and Pitt, 1988.

must also be treated prior to discharge. The discharge levels for oil from bilge water is 15 ppm, while that for ballast water is 15 ppm if the water is discharged in coastal waters and 100 ppm if the water is discharged in the ocean (Parker and Pitt, 1987).

The criteria laid out by the International Marine Organization (IMO) for oil in water monitors specify that all types of oil must be measurable within 10 ppm or 20% or whichever is greater for ballast and bilge monitors, and 5 ppm at 15 ppm for bilge alarm monitors, even when mixed with solids or entrained air. In addition to the analytical aspect, the monitors must be able to withstand the harsh marine environment, be simple, safe and reliable, must not clog in the presence of oil surges, and must provide alarms and controls so that appropriate oil removal equipment is shut down when the discharge limit is exceeded.

Commercial oil in water monitors using the principles of light scatter, turbidity, solvent extraction/light adsorption are available for bilge and ballast water. Table 14 illustrates the advantages and disadvantages of the principles of operations of these oil in water monitors. Of these methods, monitors based on the light scatter method are felt to be the most reliable and simplest for the bilge and ballast water monitoring in providing the accuracy requirement of 5 ppm. This is reflected in the relatively high proportion of commercially available monitors using the light scattering principle, as illustrated in Table 15.

TABLE 14. PRINCIPLE OF OPERATION OF COMMERCIALLY AVAILABLE OIL IN WATER MONITORS

DETECTION PRINCIPLE	SAMPLE CONDITIONING	ADVANTAGES	DISADVANTAGES
Ultraviolet flourescence	uniform particle size	high sensitivity	sensitivity depends on aromatic content of oil. Recalibration often required. Solids mask oil droplets, high concentrations give low readings.
Ultraviolet absorbance	uniform particle size	high sensitivity, fast response time	not robust, deaeration necessary, aromatic content variability, windiw cleaning problems, affected by solids with small optical path length
Light scatter	uniform particle size	high sensitivity, fast response time, simple and robust, no recalibration for oil type needed. Can be made to minimise clogging	solids interferences (which may be overcome by ultrasonic differential techniques or detection at different angles and intelligent signal processing)
Tape evaporation	spray on tape and heat	high sensitivity, similar performance for various oil types	clogging of tape, slow response at low concentrations, relatively complicated, solids interference
Solvent extraction/ infrared	dissolve oil in solvent and separate	high accuracy, low difference in oil sensitivity, detects dissolved oil	requires use of solvents, slow response time, not robust, solids affect readings by interfering with solvent separation
Infrared absorption	deaerators, no solvent used for measurement in water at 3.4 um	direct measure of hydrocarbon peak	small optical path length can lead to clogging problems, accuracy difficulties since the oil absorption peak coincides with a sharply rising water background absorption

TABLE 15. SUPPLIERS OF OIL IN WATER MONITORS

MANUFACTURER	ADDRESS	MODELS	PRINCIPLE OF OPERATION
Babcock-Bristol	Croydon, Surrey, UK	OTM	uv fluorescence
		OTM 18	Multiple angle light scattering
		OTM17 XA	Multiple angle light scattering with centrifugal separator
		Mark II	
		OPM1	Light scattering
Biospherics Inc.	Rockville, Md, USA	BA-200 OILARM OS100M Oil Sentry	Light scatter with push-pull cleaning mechanism
Fellow Kogyo	Toyko, Japan	FOCAS-1200	White light scatter with ultrasonics for particle discrimination
Horiba	Kyoto, Japan	OCMA-34	multiple angle light scatter
ITT Corp.	Dordrecht, Netherlands	OILCON	Multiple angle light scatter
Monitor Technology	Redwood City, CA., USA	Monitek 160/829	Turbidity
Quantek	Tulsa, OK, USA	Mark VII	Infrared light scatter
		Mark VIII	" " "
		Mark V-e	" " "
		Mark V-n	" " "
Sahkolikeiden	Hamburg, Germany	OILI S1000	Infrared absorption
Salen and Wicander	Sundyberg	MARPOIL	Multiple angle light scatter with sample drawn into gas tight box in engine room

TABLE 15. (cont'd) SUPPLIERS OF OIL IN WATER MONITORS

MANUFACTURER	ADDRESS	MODELS	PRINCIPLE OF OPERATION
Separation Recovery Systems	Irvine, CA. USA	BA-1 OCA ECC	White light scatter
SERES	Les Milles, France	ODME-S663	Multiple angle laser light scatter with separator for particulate discrimination
Shimadzu	Kyoto, Japan	ET15B ET-25 ET-30 ET-30M	LED with scatter with ultrasonics for particle discrimination
Yamatake-Honeywell	Tokyo, Japan	OIL-A-LYSER	LED light scatter with ultrasonic for particle discrimination

Adapted from Parker and Pitt, 1988.

There is considerable flexibility in the IMO regulations with respect to the method of detection and quantification, (i.e. acceptable principles range from light scatter to UV adsorption, ir adsorption etc.) as long as the basic requirements of operability are adhered to. All these methods require use of an appropriate calibration standard. Because of the various principles of operation, the oil measured from various shipboard discharge will not be comparable.

Commercially available portable oil in water meters for field monitoring of oil and grease and batch sampling and analysis also includes the Horiba OCMA-200, the Miran 1FF Fixed Filter Laboratory Analyzer, the Shimadzu Type POC-100 Portable Oil Content Meter and the Turner Spectronic Meter. All these meters quantify the oil and grease content spectrophotometrically and require extraction of the oil and grease components into an appropriate solvent prior to quantification. A comparison of the Horiba, Miran and Turner Spectronic meters was made by Rewick, 1981. The results, shown in Table 16, indicated that the Miran model provided the highest reproducibility having an average deviation of 5 ppm. The Horiba, Miran and Shimadzu meters all use infrared adsorption for quantification, while the Turner Spectronic uses adsorption at a wavelength in the visible and near UV region (620 nm for No. 6 fuel oil and 340 nm for No. 2 fuel oil). Solvents used for the Horiba, Miran and Shimadzu are carbon tetrachloride and Freon, depending on the ease of solubility of the oil in the wastewater. The Horiba also incorporates a solvent extraction chamber, for extracting the oil

TABLE 16. COMPARISON OF OIL IN WATER MONITORS

	INSTRUMENT TYPE		
FEATURE	HORIBA	MIRAN	TURNER
Weight (kg)	8.9	6.5	7.4
Wavelength (nm)	3400 - 3500	3400 - 3500	620 for No. 6 oil 340 for No. 2 oil
Solvent	CCl_4 or Freon	CCl_4 or Freon	$CHCl_3$
ppm oil measured directly on scale	0 - 100	0 - 3500	0 - 4000
Oil analysis (ppm)*	1. 592 ± 12	588 ± 5	656 ± 16
	2. 640 ± 12	552 ± 6	676 ± 5
	3. 656 ± 10	648 ± 6	664 ± 0
	4. 490 ± 40	536 ± 0	582 ± 2
	5. 562 ± 10	488 ± 0	478 ± 2
	6. 516 ± 10	576 ± 10	526 ± 14
Average deviation	± 16	± 5	± 7

Note: * Oil-in-water samples from six different EPA dispersant effectiveness tests were analyzed on all three instruments. Each test was duplicated, and the average and the deviation are reported.

Adapted from Rewick et al., 1981.

and grease components from the wastewater while the others require solvent extraction prior to detection.

Actual operating data for the above monitors are not available. The Horiba oil content meter has been tested on oilfield produced waters in Alberta; however, its use has been abandoned for excessive fouling and deposits on the sample chambers (WTC, 1988). Further research with respect to an assessment of actual experience with such instruments would be extremely useful in minimizing the limitations of the present analytical methods for determining oil and grease in water.

9 CONCLUSIONS AND RECOMMENDATIONS FROM LITERATURE REVIEW

1. The literature review on oil and grease indicated that oil and grease has been defined as any material recovered as a substance soluble in trichlorotrifluorethane. For this reason, the oil and grease parameter is non-specific, encompassing a group of substances whose only common property is solubility in the designated organic solvent, trichlorotrifluoroethane, commonly known as freon (APHA, 1985). These compounds tend to be hydrophobic and exhibit partial or total immiscibility in water. Hence, it is generally accepted that oil and grease refers to hydrophobic organic materials derived from both animal and vegetable sources and petroleum. However, this way of defining oil and grease poses several dilemmas : (i) some materials not considered to be oil and grease will also be dissolved and (ii) freon may not be an appropriate solvent for certain types of oil and grease. Therefore, the method is often modified (particularly with respect to solvent choice) to improve the recoveries of oil and grease from the water. These modifications make comparison of oil and grease values difficult.

2. The two origins of "oil and grease" in water and wastewaters are quite different; the oil and grease derived from animal and vegetable origin are comprised of a specific group of organic compounds - long chain - fatty acids while the oil and grease derived from petroleum cover several groups of organic compounds (straight-chain aliphatics, simple

aromatics and polyaromatic hydrocarbons). The numerous compounds associated with the petroleum based "oil and grease" have a wide range of environmentally relevant properties (compared to the single group found in with the animal and vegetable based oil and grease). Therefore, the petroleum hydrocarbons pose more of an enviromental hazard to organisms than animal and vegetable based oil and grease. In addition, the standard methods for determining oil and grease are less likely to be able to accommodate the wider range of organic compounds found in petroleum based oil and grease.

3. The reasons for monitoring oil and grease include:
   (i) prevention of process upsets in oil removal operations in wastewater treatment so that release of oily water discharges in excess of the regulated amounts to the receiving water are minimized
   (ii) prevention of operational upsets, caused by releases of oil, to downstream process operations
   (iii) determination of whether surface water quality objectives are being met
   (iv) regulation of oily water discharges of final effluents by governmental agencies
   (v) assessment of the fate and effects to organisms.

These monitoring applications cover a concentration range over several orders of magnitude (< 1 mg/L to several thousand mg/L). Each application has specific problems in the determination of oil and grease. These problems include

(i) difficulties in sampling, (ii) the ability of standard methods to detect the concentration range of interest and (iii) the ability of the standard methods to accurately reflect the part of the oil and grease parameter that is of interest.

4. Oil and grease consists of a dissolved portion and an immiscible portion. The immiscible portion may be present as (i) a free floating layer, (ii) a suspension of large droplets or (iii) a suspension of finely emulsified droplets or (iv) a combination of all three. This immiscibility and tendency to rise presents difficulties in the collection of a representative sample, depending on the amount present and the level of turbulence in the system. Precautions during sampling are required at all concentrations; however, practical limitations generally dictate and restrict the collection of a representative sample. However, in the collection of samples having low oil and grease concentrations, sample homogeneity is more likely since the oil and grease will be present as finely emulsified droplets and/or dissolved. Because of sample homogeneity, concentration of the oil and grease components from large volumes by an on-site method would allow gravimetric determination of oil and grease at low concentrations (<25 mg/L).

5. There are currently three standard methods used for the determination of oil and grease: the partition-gravimetric method, the partition infrared method and the soxhlet

extraction method. Of these, the most widely used method is the partition-gravimetric method. However, this method can only detect concentrations greater than 25 mg/L, since the relative experimental errors in the quantification step by gravimetry becomes large. Use of larger sample volumes would alleviate this problem, however, collection, transportation and handling of these large volumes (>1 L) becomes cumbersome. Although the partition-infrared method can detect below 1 mg/L, it is appropriate only when a reliable calibration standard is used. The soxhlet extraction procedure is used for samples having a concentration greater than 100 mg/L. Hence, there is a need for a method for monitoring applications where the concentrations of oil and grease are low.

6. The oil and grease, as determined by the standard methods is a combined measure of both the dissolved and the immiscible portions. However, in some applications, only the immiscible portion is relevant, as in the monitoring of oil removal processes which remove only free oil. In these cases, if the dissolved fraction is high relative to the immiscible fraction, the value obtained will not reflect the actual oil removal effectiveness of the unit. This point is important in the determination of best practicable technology by regulatory agencies. In other cases, such as in biomonitoring applications, both fractions are important in order to assess their individual effects. Distinction of these two fractions is therefore needed.

Based on these findings, there is a need for the following:

1. A better definition of oil and grease be established to make the value more relevant. If the current definition (i.e. materials soluble in a designated solvent) is maintained, then a data base be developed, with the intent of specifying suitable solvents for given types of wastewater. This would probably aid in standardizing the methods within similar wastewater types.
2. The various reasons for monitoring oil and grease should be reflected in the standard methods for determining oil and grease.
3. Improving the detection limit of the partition-gravimetric method be made in view of its widespread use, and relatively easy technique.
4. In order to improve the detection limit of the partition gravimetric method, larger sample volumes need to be collected. Therefore, some form of concentration or isolation methods needs to be be developed during sample collection.
5. Modifications should be incorporated in the standard methods for determining oil and grease to recognize individually, the dissolved and suspended fractions of oil and grease.

This section reviews concentration and isolation methods used for trace organics in water analysis and their suitability for oil and grease analysis at low concentrations.

The range of concentrations of hydrocarbons in these types of water is shown in Table 17. The total hydrocarbon concentration is generally less than 15 mg/L, and may include dissolved and particulate matter (some of which may be caused by oil and grease, depending on the sample). Specific organic compounds will however have concentrations in the micrograms/L range. To increase the sensitivity of the analytical method, the sample must either be concentrated by several orders of magnitude or the organic compounds themselves must be isolated prior to quantification.

Criteria for method selection for oil and grease analysis should therefore include:

(i) the ability to allow on-site sampling so that losses during handling and transportation may be minimized
(ii) the ability to concentrate/isolate components of oil and grease, (i.e. non-polar hydrophobic compounds as discussed in Section 3)
(iii) the ability to handle both finely dispersed and dissolved fractions of oil and grease
(iv) the ability to provide good recovery of the oil and grease components
(v) the ability to allow routine analysis requiring little time and/or attention.

TABLE 17. TYPICAL CONCENTRATIONS OF HYDROCARBONS FOUND IN AQUEOUS SYSTEMS

SYSTEM	CONC. ug/L	ANALYTICAL METHOD	REFERENCE
Seawater			
English Channel	1.1-1.7	uv flourescence using Ekofisk oil as reference	Bayne et al., 1981
Irish Sea	2.1-3.5	"	"
Thames Estuary	43	"	"
Mersey Estuary	74	"	"
Refinery Effluent	10-700	neutral fraction, soluble in DCM,GC/MS analysis	USEPA, 1978
Municipal Effluent[1]	1.5-2.1	hexane and DCM solubles of filtered samples, TLC and microgravimetric analysis	Eganhouse and Kaplan, 1982
"	8-12.3	same as above, unfiltered sample	"

Notes: [1] - Units are in mg/L

GC/MS - gas chromatography/ mass spectroscopy
TLC - thin layer chromatography

10.1 Concentration Methods

In concentration methods, a considerable portion of the water is removed and the dissolved substances are left behind in concentrated form. Typical operations are freeze concentration, vacuum distillation and membrane processes such as reverse osmosis and ultrafiltration.

10.1.1 Freeze concentration

In freeze concentration, a portion of the water sample is frozen, forming pure ice. The unfrozen portion then becomes concentrated in dissolved materials. This method has been tested extensively by Baker (as cited by Baker, 1970) for the concentration of pure organic materials in water. Factors investigated included freezing in several stages, the effect of mixing, the nature of the organic solutes (dissociation potential, molecular weight, effect of substituted groups) and the presence of dissolved inorganic salts. Compounds tested included phenol and substituted phenols, volatile fatty acids, and acetophenone. Up to 80% recovery of m-cresol (at an initial concentration of 310 ppm) was obtained with a 20-fold volume reduction. The volume of samples tested was 200 mL.

High concentrations of inorganic salts produced low recoveries of the organic compounds since the dissolved salts interfered with ice crystal formation and caused the solute rich liquid to be entrapped in the ice crystals.

Sorption of the insoluble nonpolar organics on the ice formed result in poor recoveries for these types of organics (Lenheer, 1980, citing Schaumberg, 1974). The process is relatively slow and the sample volumes are limited as only up to a maximum of 500 mL can be used. Therefore, freeze concentration would not a suitable candidate for oil and grease analysis because (i) the nonpolar organic compounds of interest would not be recovered in sufficient amounts, (ii) high TDS levels present in some wastewaters (oilfield produced water) would interfere and (iii) the time required would make it unsuited for routine analysis.

10.1.2 Vacuum distillation

In vacuum distillation (or evaporation processes), the sample is boiled at reduced pressure and at ambient or near ambient temperature until sufficient water is driven off to produce a sample concentrated enough for the subsequent analysis. This method is most suited for polar, non-volatile organics (Lenheer, 1980). Therefore, vacuum distillation would be unsuited for oil and grease samples, which may contain a substantial amount of volatile components as previously discussed. Most of these volatile components would therefore be lost during the evaporation of relatively large sample volumes (>> 1 L) used in oil and grease analysis.

10.1.3 Membrane processes

Membrane processes which may be suitable for oil and grease analysis are microfiltration, ultrafiltration and reverse osmosis. In these processes, the feedstream is pumped tangential to the surface of a porous membrane. The suspended material (and in the case of reverse osmosis, inorganic solutes as well) is rejected away from the surface of the membrane and the water permeates through the membrane. Thus a concentrated stream is left behind.

The membrane type used depends on the process used. Microfiltration membranes are available in polymeric materials such as polypropylene and inorganic materials such as ceramic and stainless steel. Microfiltration membranes having pore diameters as low as 40 angstroms are available (Hsieh, 1988). Ultrafiltration and reverse osmosis membranes are available in cellulose acetate, cellulose triacetate and other polymers such as polysulfones, polyamides and polyvinyl alcohol (Sourirajan and Maatsura, 1985). For reverse osmosis membranes, the membrane pore diameters are less than 10 angstroms (i.e. in the ionic size range). For ultrafiltration membranes, the pore diameters are rated in terms of molecular weight cutoff with 500 being the lowest. The water flux (flow rate per unit area) is greatest with microfiltration followed by ultrafiltration and reverse osmosis.

Cross-flow microfiltration and ultrafiltration may be useful for oil and grease analysis, particularly for the separation of free and emulsified oil from dissolved oil. The diameter of the emulsified oil droplets would generally be larger than that of the pore diameters and would be retained in the concentrate. Ultrafiltration is actually used at an industrial scale for removal of oil from metal cutting wastewaters to concentrate the emulsions and reduce the effluent oil discharges (Sonksen et al., 1978, Davies, 1985). Cross-flow microfiltration has also been applied to the treatment of oil in water (Tanny and Hauk, 1980). The process has proven to be successful in removing oil to very low concentrations (<10 mg/L). It therefore, seems possible that cross flow microfiltration and ultrafiltration could be used for concentration of samples for oil and grease determination, having the benefit of being able to act as a filter for suspended solids as well. However suitable operating conditions such as pressure and flowrate must be determined to ensure that adequate water flux and sufficiently high recoveries of oil and grease are obtained.

Reverse osmosis has been tested on herbicide samples (2,4-D) by Edwards and Schubert, 1974, and by Klein et al., 1975, on trace organic contaminants in drinking water. The latter researchers evaluated cellulose acetate, cellulose triacetate and ethyl acetate membranes. They found that hydrophobic solutes of low water solubility were retained by on the membrane surfaces by physical sorption. Ionizable volatile fatty acids were retained in the concentrate in the greatest quantity, while low molecular weight esters, aldehydes, ketones, phenols and alcohols were retained in the least quantity. Membrane type is very important in determining which organics are rejected and retained in the concentrate stream rather than be adsorbed onto the membrane material. McKinney, 1972, found that better rejection of organics was obtained with polyamide membranes compared to cellulose acetate membranes.

It may be possible to desorb the organic solutes from the membranes provided that the membrane is compatible with the solvent used for desorption. Also the sample must be relatively clean of suspended materials since membrane fouling will cause the loss of water flux through the membrane and limit the sample volume that can be processed.

Equipment is available for applying cross flow microfiltration, ultrafiltration and reverse osmosis for oil and grease analysis. Stirred cells (1 L) in stainless steel are commercially available and can be readily adapted for oil and grease analysis for batch concentration. Alternatively for larger samples, it would be possible to continuously concentrate the sample using a tubular configuration and a pump. Therefore on-site concentration would be feasible with both configurations.

The main benefits of using a membrane system would be little loss of volatile organics since no heat is involved. Very high degrees of concentration could also be obtained. Therefore, a combination of membrane processes would provide a good way of obtaining fractionated components of oil and grease (suspended and dissolved). If membrane materials are found to be compatible with the solvent it is quite feasible for the solvent extraction to be carried out in the same vessel, as many of the commercial equipment is fitted with magnetic stirrers. The solvent could then be taken to the laboratory for further analysis (by infrared analysis or gravimetry). Testing of these processes for oil and grease analysis is therefore warranted.

10.2 Isolation Methods

Isolation methods extract the organics from the aqueous phase by solvent extraction or adsorption on activated carbon or polymeric resins.

10.2.1 Solvent extraction

The use of solvent extraction for increasing the sensitivity of the analysis of oil and grease in water is possible only if large volume extractors are available. However, transport of large volumes to the laboratory will still be required. Lenheer (1980) cited various continuous extractors of Goldberg et al., (1977), Wu and Suffet (1977). These extractors are capable of operating at flow rates of up to 8 L/h with a variety of different solvents. An apparatus invented by Ahnoff and Josefsson (1974), as cited by Bjorseth, A. and G. Angellitti, (1981), can be used in-situ, thereby eliminating the need to transport large volumes to the laboratory. Solvent extraction is the basis for the standard methods for oil and grease analysis. Therefore, this process is suited for oil and grease analysis. However, specialized equipment is required and this makes it less likely to be adopted as a routine type of analysis.

10.2.2 Sorption

Sorption processes include adsorption (solute is bound at the substrate surface) and adsorption. The substrates available for sorption includes activated carbon, styrene-divinyl- benzene copolymers, phenol-formaldehyde copolymers, methylmethacrylate ester polymers, polyamide (Nylon), polyurethane foam, and C_{18} bonded silica. There are several mechanisms for bonding: hydrophobic effects, pi electron interactions, and hydrogen bonding. Sorbents with more bonding mechanisms, while allowing good sorption of organics, are unsuited for analysis since desorption will be difficult.

Commercially available sorbents are activated carbon, XAD resins, polyurethane foam and octadecylsilane bonded materials.

10.2.2.1 Activated carbon. In the activated carbon process, the water sample is passed through a column of activated carbon, which adsorbs the dissolved organic compounds from the aqueous phase. The compounds are then desorbed from the activated carbon by eluting with a suitable organic solvent. Units available to handle many thousands of gallons are available. This process is very common in the analysis of organic compounds in water (Jolley, 1980).

The carbon adsorption method of isolating organic matter from water is also incorporated in ASTM Method D2910 - 85 (ASTM, 1987). This procedure stipulates the use of 10 to 20 g of carbon, and a flowrate sufficient to provide a residence time of 2 minutes. The organic matter is recovered from the activated carbon by soxhlet extraction using an assembly as shown in Figure 12. The solvent recommended is a mixture of 38 parts of propylene dichloride and 62 parts by volume of anhydrous methanol. At least 8 hours of extraction time is recommended using a siphon recycle time of about 1 h. The choice of solvent for the ASTM method was based on solvent extractions of phenol, standard ABS, dichlorophenol, dinitro ortho secondary butyl phenol and sodium dinitro ortho secondary butyl phenate. Other solvents tested were chloroform, and methanol (following chloroform). The propylene dichloride/methanol produced higher recoveries compared to the chloroform and methanol solvents.

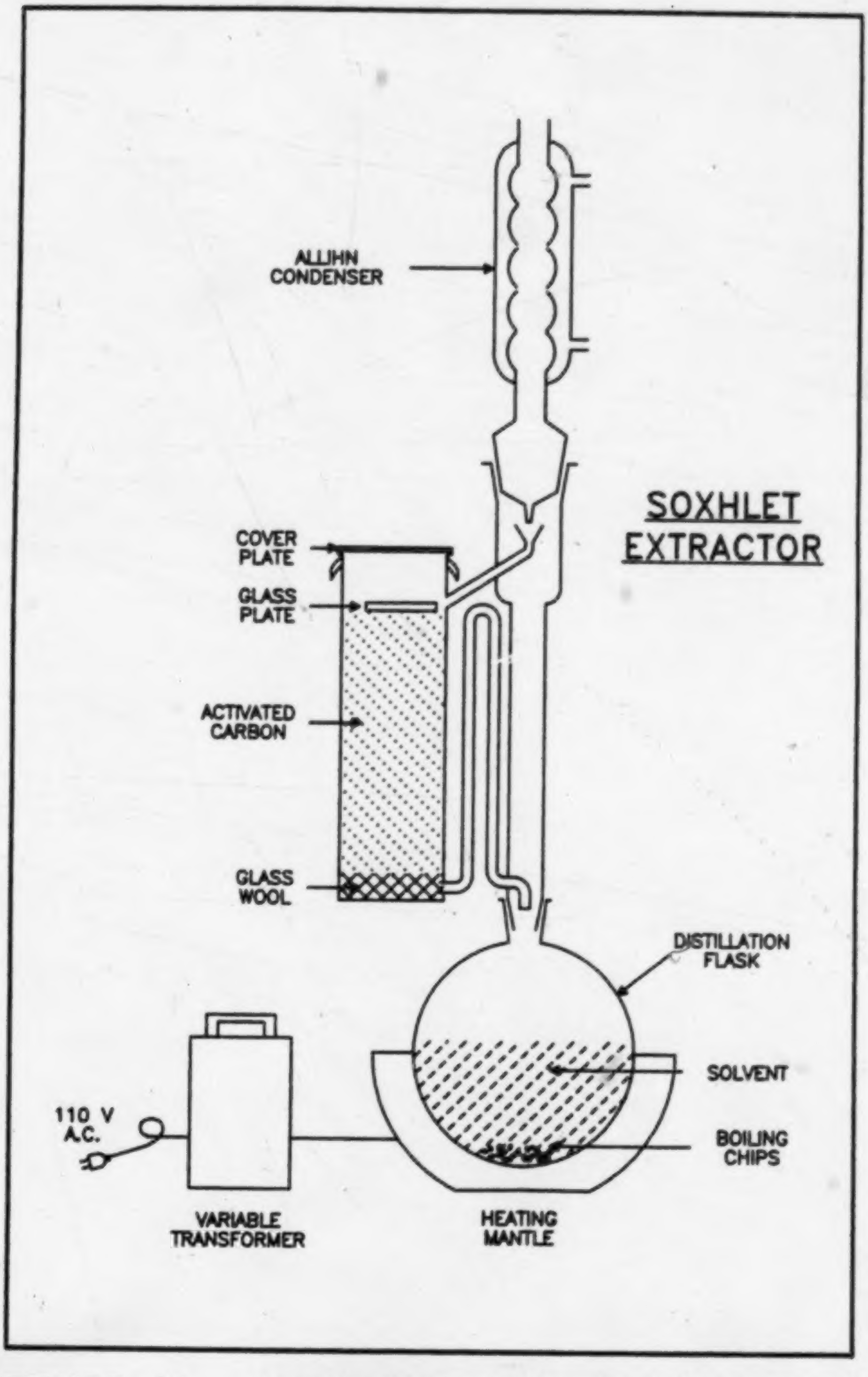

ALLIHN CONDENSER
SOXHLET EXTRACTOR
COVER PLATE
GLASS PLATE
ACTIVATED CARBON
GLASS WOOL
DISTILLATION FLASK
SOLVENT
BOILING CHIPS
110 V A.C.
VARIABLE TRANSFORMER
HEATING MANTLE

FIGURE 12: APPARATUS USED FOR RECOVERY OF ORGANICS IN WATER USING CARBON ADSORPTION

With an actual wastewater water sample, the propylene dichloride/methanol solvent combination recovered 35% more than a chloroform/methanol combination (as determined gravimetrically). For a river water sample, the propylene dichloride/methanol solvent combination produced a 55% higher recovery than the chloroform/methanol solvent combination. The weight of organics recovered was about 2240 mg for the wastewater sample and 1400 mg for the river water. Volume data was not given.

Lee and Walden (1970) used a combination of Filtrasorb-400 and Darco 6-60 activated carbon to analyse kerosene in water. Activated carbon (0.2 g) was mixed with 1 L samples of water samples containing kerosene. The activated carbon was then filtered and washed with 3 mL of acetone five times. The acetone was then diluted with 10 mL acid lauryl sulphate. The resulting turbidity obtained when the acetone was mixed with the acid lauryl sulphate, a surfactant, was found to be proportional to the concentration of kerosene in the acetone. The optical density of the surfactant/acetone mixture was measured at 550 mμ. A concentration level down to 10 mg/L was detectable and 95% recovery of the kerosene was obtained with this method.

Lsysj (1980) used Supelco activated carbon tubes (150 mg) to adsorb volatile aromatic hydrocarbons in seawater and offshore produced water. 850-1000 mL seawater samples were collected using a depth sampler. The samples were then sparged with nitrogen at a rate of 500 mL/min to strip the volatile acids from the seawater. One mL of carbon disulfide was then used to desorb the organics, and the solvent was then analysed by gas chromatography. The levels of volatile aromatic hydrocarbons were found to range from 2.1 to 41 µg/L (in water). The recoveries for known samples containing benzene and toluene were 82%±5% and 85.4%±3.5% respectively at a concentration of 0.5 ppb. In contrast however, the recoveries of m-xylene and o-xylene were considerably less, corresponding to 61.4%±5.4% and 39±5.4%, respectively.

Jolley (1980) noted however, that the major disadvantage of the carbon adsorption method is that recovery of organics may not be complete using soxhlet extraction based on the use of chloroform and ethanol solvents. However, this may be in part a result of the solvent used, as the ASTM solvent comparison data shows. Jolley (citing Modell et al., 1980) suggested supercritical liquid carbon dioxide as a solvent. An alternative solvent is the sequential use of dioxane and dimethylformamide (Jolley, 1980, citing Fuchs and Kuhn, 1975), based on comparative tests with other solvents (chloroform, dioxane, ethanol and acetone.)

The high affinity of dissolved components of the oil and grease to the activated carbon makes it more difficult for desorption of these compounds. Chriswell (1978) obtained poor recoveries of alkanes (dodecane, hexadecane, octadecane, eicocosane, and tetradecane) (<28%) when Filtrasorb 300 was used to analyse for model organic compounds. These compounds remained in the water and were not adsorbed. Similar low recoveries were obtained with the aromatics such as dimethylnaphthalene, acenaphthalene and phenanthrene. However, unlike the alkanes tested, only 20% of these compounds remained in the water phase. The activated carbon has a high affinity for these types of organics, making subsequent desorption difficult. The method of desorption was column elution with a mixture of chloroform and diethyl ether. Presumably with a more intense mode of desorption, these recoveries could be improved.

10.2.2.2 Polyurethane foam. Polyurethane foam has been used for the removal of oil slicks in oil spill situations (Will and Grutsch, 1971). Polyurethane has been applied in the analysis of organics compounds including nitrogen-containing organics, (aniline and aminophenols) and polyaromatic hydrocarbons (Denton et al., 1980 citing several authors.)

Denton et. al, 1980 used open pore polyurethane for the adsorption of phenols from coal wastewaters. Open pore polyurethane is a foam produced by reacting a polyaryl-poly-alkylene-polyisocyanate with a polyol in the presence of a catalyst. The foam produced is made of an agglomeration of spherical particles with uniform diameters of 1 to 10 microns.

Various types of polyurethane were formulated, with particle sizes ranging from 2.7 to 4 microns. Synthetic solutions containing phenol and 3,4-xylenol at a total phenol concentration of 112 mg/L were passed through a column of in-situ formed open pore polyurethane at a flow rate of 38 mL/min. The open pore polyurethane adsorbed the phenol more effectively than XAD-2 resin and activated carbon as indicated by the early breakthrough of phenols by the latter two adsorbents. The elution of the open pore polyurethane using methanol was also more effective.

Webb, 1975 tested polyurethane foam for paper mill wastewater components and fuel oil. Water samples were passed through a foam plug fitted in a column. The synthetic papermill wastewater contained 5 mg each of camphor, fenchone, fenchyl alcohol, alpha-terpineol, guaiacol, phenol and para cresol. No more than 10% of these compounds were however extracted by the foam. Lower amounts of each compound (20 µg/L) were also tested, with no improvement. Increasing the contact time by soaking in shaking for several hours in a jar containing cresol solution did not improve the extraction.

The polyurethane did not extract dispersed oil from a 1.6 mg/L No. 2 fuel oil dispersion. Polyurethane coated with DC-200, used in gas chromatography for liquid phase adsorption, did remove 80% of the oil from the water. However, only 34% could be recovered from the polyurethane plug by elution with carbon tetrachloride.

The main advantage of foam adsorbents is the ability to process large volumes of water. Flowrates up to 250 mL/min have been used by Saxena et al, 1972, as cited by Lenheer, 1980. Leenheer, concluded that polyurethane foams were good adsorbents for PCB's, PAH, and certain organochlorine pesticides in low-turbidity water. The main advantages are high flow rate application, convenience of use and low cost.

Despite the relative success with other organic solutes, the work by Webb suggests that polyurethane foam is unlikely to be suited for oil and grease analysis, because of its inability to adsorb the components of the fuel oil dispersion. This sample is most representative of the oil and grease in water and unless the oil and grease components have a large proportion of polyaromatic hydrocarbons, the use of polyurethane foam for oil and grease analysis would be limited to dissolved oil and grease only.

10.2.2.3 Polymeric resins

The use of polymeric resins is also based on adsorption of the dissolved organics from aqueous media. The most common polymeric adsorbents used are the XAD resins (produced by Rohm and Haas). The XAD resins are porous, spherical polymeric adsorbents which have a high affinity for dissolved organics in aqueous media. There are 5 types of XAD resins : XAD-2,-4,-7,-8, and -16. The XAD-2 and XAD-4 resins are made of a styrene-divinyl benzene copolymer, while the XAD-7 and XAD-8 resins are made of a polymethylmethacrylate copolymer. The XAD-16 resin is made of polystyrene. Rohm and Haas also markets Duolite S-761 resin which is made of a phenolic polymer. The properties of these resins are highlighted in Table 18.

The XAD-2 and XAD-4 resins are particularly suitable for solutes with lipophilic or hydrophobic properties (Lenheer, 1984) while the XAD-7 and XAD-8 resins are more suited for polar organic solutes. The following paragraphs therefore, focus on the potential use of XAD-2 and XAD-4 resins for oil and grease analysis.

TABLE 18. XAD RESINS - TYPES AND PROPERTIES

GRADE	CHEMICAL NATURE	POROSITY Volume %	TRUE WET DENSITY, g/cm^3	SURFACE AREA, m^2/g	AVE. PORE DIAMETER, angstroms	SKELETAL DENSITY g/cm^3	MESH SIZE
XAD-2	polyaromatic	42	1.02	300	90	1.07	20 - 60
XAD-4	polyaromatic	45	1.02	725	40	1.08	20 - 60
XAD-7	acrylic ester	55	1.05	450	90	1.24	20 - 60
XAD-8	acrylic ester	52	1.09	160	225	1.23	20 - 60
XAD-16	polyaromatic	na	1.02	800	100	1.08	20 - 60
Duolite S-761	phenolic	na	1.11	300	600	1.24	16 - 50

Adapted from Rohm and Haas Co., 1985.

The average surface area of XAD-4 resin is more than double that of XAD-2, and has a smaller pore diameter. The pore diameter dictates the size of molecule which can be adsorbed. Gustafson (1968) recommended that sorbate size be at least six times that of the diameter of the solute molecule adsorbed.

The major advantages of the resins for isolation of organics from water are controlled pore size which allow rapid rates of solute diffusion within the beads, high internal surface areas, and low-pressure, high flow rate column packing available. Changing the pH conditions of the bed by passing acid or base allows fractionation of organic solutes. Desorption of the sorbed organics is relatively easy compared to activated carbon; in many cases, desorption is accomplished by passage of the organic solvent through the bed. Fractionation of organic solutes into acid, neutral and base extractables is also possible.

XAD resins have been used for the analysis of low concentrations of organics in drinking water and river water, as well as for the removal of dissolved organic pollutants. The procedure used for the analysis of organics in water usually consists of passing the water through a column of cleaned, packed resin. After a sufficient volume of water has been passed through the column, an organic solvent is then used to desorb the organic compounds from the resin surfaces. The following paragraphs highlight some important operating conditions and typical problems encountered in the use of XAD resins with particular emphasis on the organics found in oil and grease containing waters.

Junk (1974), conducted an extensive study of XAD resins for a wide range of compounds, and investigated the effects of compound class, bed operating conditions (pH, column height, flowrate), resin type and eluting solvent. The objectives of Junk's work were to isolate representative dissolved organic impurities on polymeric resin, to recover these organics by elution with appropriate solvent and to concentrate the solvent so that the organics could be quantified by gas chromatography. XAD-2, and XAD-4 resins were used. The compounds tested ranged from non-polar hydrocarbons found in oil and grease including polynuclear aromatics (naphthalene, 2-Methylnaphthalene,1-Methylnaphthalene, biphenyl, fluorene, acenaphtene, tetrahydronaphthalene) and, alkyl benzenes (ethylbenzene, cumune, p-Cymene) and organic acids (octanoic acid, decanoic acid, palmitic acid and benzoic acid). Other more polar compounds included alcohols, aldehydes and ketones, esters, ethers and phenols. Halogenated and nitrogen compound were also tested. Concentrations of organics ranged from 10 to 100 ppb.

Recoveries of the polynuclear aromatics which are found in petroleum type wastewaters ranged from 62% for tetrahydronaphthalene to 101% for biphenyl. Recoveries of other polynuclear aromatics listed above were over 83%. Organic acid recoveries under acidified conditions were 100% (except for decanoic acid recovery which was 90%). Under unacidified conditions, the recoveries of the organic acids were poor. Other more polar compounds (such as undecanone, acetophenone, benzophenone and benzaldehyde) which may also be present in oily wastewaters also gave good recoveries (greater then 90%). There was no difference in recoveries when either XAD-2 or XAD-4 was used, and the recoveries were therefore reported without distinguishing resin type.

The resin cleanup procedure was found to be quite important. In blank tests, the resins leached naphthalene, ethyl-benzene and benzoic acid which are products of the bead formation process. The most effective cleanup procedure was found to be a sequential Soxhlet solvent extraction with methanol, acetonitrile and diethyl ether, followed by storage in methanol. Other cleanup methods tried were vacuum degassing at 225°C under 10^{-7} torr and heat desorption in an inert gas train at 200°C, but these were not as effective as Soxhlet solvent extraction. It was also necessary to keep the resin in a wetted state since cracking of the resin would release further amounts of impurities.

Webb (1975) tested XAD resins on a broad range of individual organic compounds representative of paper mill wastewaters, dissolved fuel oil and textile dyes. Organics detection was by gas chromatography. XAD-2,-4,-7 and -8 and combinations of XAD-2 and -4, XAD-2 and -7 and XAD-2- and -8 were used. The test solution consisted of bis-chloro isopropyl ether, cis-trichloroethane, n-hexadecane, alpha-Terpineol, naphthalene, o-nitrotoluene, 1- and 2-methyl naphthalene, benzothiazole, phenol, p-cresol, acenaphthene and dibenzofuran, each at a concentration of 50 µg/L. Solvent extraction using chloroform was also conducted on a similar mixture. Significant amounts of phenols passed through the resin columns, however the recoveries obtained with the resins was higher for the less polar compounds compared to direct solvent extraction. Hexadecane was not adsorbed, as well as alpha-terpineol and dibenzofuran.

Air drying of the resin after water passage for 3 days produced 12% lower recoveries than immediate extraction of the wet resin.

In tests where dispersions of No. 2 fuel oil in water were passed through the resin, no adsorption of the straight chain alkanes was obtained.

The main findings of Webb's work were:

(i) extensive pretreatment of the resin by washing large batches in a column with acetone, methanol and either chloroform or methylene chloride was required. Batch extraction in shake flasks was not as efficient.

(ii) a flow rate of 4 bed volumes per minute produced a greater extraction efficiency than 12 bed volumes per minute

(iii) direct elution with chloroform or carbon tetrachloride was not efficient.

(iv) treatment of the column with acetone or methanol prior to adding the chloroform or diethyl ether, was found to be more efficient.

Stepan and Smith (1977) highlighted some precautions when using XAD resins. They examined the effects of sample temperature, flow rate, pH, temperature and length of the column.

Compounds evaluated were naphthalene, phenol, o-cresol, ethyl benzene, cumene, octanoic acid, o-chlorophenol, and n-hexane in the ppm range. XAD-2 and XAD-7 resins were used. XAD-2 resin is considered to have a low polarity while XAD-7 has a medium polarity (Stepan and Smith, citing Gustavson and Paleos, 1969).

The amount of resin used was 2 g packed in a column or coil. The resins were cleaned by sequential 6-h soxhlet extractions with methanol and diethyl ether. 30 mL of diethyl ether were used to desorb the organics which were then analysed by gas chromatography after drying the solvent with magnesium sulphate.

Variations in flow rate within 5 mL/min of the set flowrate of 30 mL/min did not affect phenol recovery. However, an increase in flowrate (from 30 to 150 mL/min) decreased the recovery of all the compounds by as much as 50%.

Extraction efficiency of non-polar compounds such as alkyl benzene and naphthalene was not affected by pH changes. However, acidification improved the recovery of octanoic acid.

Schnare (1979) devised a column which would allow adsorption in the usual downflow manner; however, it could also be adapted to allow elution of the adsorbed organics in a mechanical wrist shaker. This was accomplished by using a column threaded at both ends, such that they could be capped for the elution stage. Organics tested were 50 to 300 mg/L dispersions of xylene, benzene, toluene, anthracene, ethyl benzene, cumene, benzothiazole, dimethoxyacetophenone, iso-valeric acid and hexadecane. The dispersions were prepared by dissolving the known weights in acetone and adding this solution to 1 L of distilled water. The solutions were passed through the column at a flow rate of 100 mL/min using gravity flow. Once 1 L of sample had been fed, the column was drained, and ether was poured into the tube. The tube was then capped and mechanically shaken for 1 h. Quantification of the organics was done by concentrating the solvent extract to 1 mL, and by gas chromatography.

Schnare found that as the polarity of the compound increased, the capacity of the resin (mg solute adsorbed per gram of resin) decreased. Hence for m-xylene the resin capacity was 42 mg/g resin, while for the most polar compound tested, isovalaric acid, the value was only 2.9 mg/g resin at pH 2. Corresponding values for benzothiazole and 3,4-Dimethoxy acetophenone were 29.5 and 6.6 mg/g resin respectively.

Increasing flowrate caused an increase in the recovery of the neutral compounds and a decrease in the polar compounds.

The batch method (i.e. mechanically shaking the resin) of elution was devised to overcome wettability problems during the elution stage in a column mode. Soaking the column with ether for 10 minutes did not saturate the bed, since pockets of air would develop. Efficient contact could only be effected by forcing the ether under pressure through the resin bed. The results of recoveries reported with this batch method were inconclusive as only two compounds were tested. The reported recovery for xylene was 46.4% vs 34.8% for the column desorption method. For benzothiazole, the difference was even less (91.9% for Schnare's method vs 90.9% for the column desorption method).

Magnetic stirring produced a much higher recovery for xylene (86.8%) than for the above two elution methods.

The behaviour of aliphatic vs aromatic compounds was also reported. Hexadecane recovery was only 12% while that of toluene was 56.5%. The poorer recovery of hexadecane was felt to be caused by poor desorption properties, whereas toluene was better desorbed.

Moore and Karasek (1984) tested the recoveries of a range of pesticides, polyaromatic hydrocarbons, phenols and phthalate esters (concentration range of 20 - 200 µg/L) from XAD-2 resins. 2 g of resin, packed in a 100 cm x 8 cm resin column, and a flow rate of 30 mL/min were used. Total solution volume was 500 mL. The elution solvent was diethyl ether, and quantification of the recovered compounds was done by gas chromatography/mass spectrometry. For the compounds tested, a pH of 7 was found to be best. XAD-2 proved to more effective than XAD-7 for recovering the non-polar compounds as typically found in oily wastewaters. For example, recoveries of biphenyl and methyl naphthalene by XAD-2 were 90% and 88% respectively while the corresponding recoveries by XAD-7 were 59% and 55%.

The extent to which organics leached from cleaned XAD-2 resins might render the procedure inaccurate was determined by Care (1982). Blank extracts obtained from passing 3 - 15 L of water through the column and solvent produced the following substances: toluene, styrene, C_2 substituted benzenes, undecane and polysubstituted benzenes. Individual amounts recovered ranged from 1 µg to 50 µg. Hence, Care concluded that there would be some uncertainty at the 0.6 ppb level.

The stability of hydrocarbons samples on XAD-2 resins was tested by Green and Pape (1987). The objective of this work was to determine the fate of typical organic samples sorbed on the XAD resin and to determine whether the samples were effectively preserved. 50 L of a 10:1 crude oil/dispersant mixture was spiked with a 1-2 L marine bacterial culture. The oil/water mixture was then passed through a 1.9 cm x 37 cm long resin column (filled with 90 mL of resin) at a rate of 200 mL/min. The concentration of the oil was 1 mg/L. Separate columns were treated in a similar fashion, however, elution of each column with successive 200 mL volumes of methanol and dichloromethane was done after a period of 0, 1, 3, 10, 32 and 100 days. The methanol was back extracted with pentane which was then combined with the dichloromethane. For comparison, samples stored in water were also extracted after similar time periods.

The stability of the samples was determined by examining the gas chromatography trace and comparing the ratios of pristane:C_{17}, phytane:C_{18}, to unresolved complex mixture (UCM):C_{18}. Pristane and phytane are branched chain isoprenoids which are not readily biodegraded compared to the straight chain alkanes.

The results showed marked degradation for the stored water samples with the gas chromatography traces showing little resolved peaks characteristics of individual alkanes. In contrast, the traces for the samples that had been sorbed on the

XAD-2 columns showed the peaks quite clearly. The ratios of pristane:C_{17}, phytane:C_{18} and UCM:C_{18} rose sharply with time, reaching 1.3, 1.6 and 6.0 after 20 days for the stored water samples. The corresponding ratios for the XAD-2 sorbed samples were less than 0.25 at 100 days, showing the superiority of the XAD-2 resin method for retarding biodegradation.

Ishiwatari and Hamani (1980) used XAD-2 resins to characterize organic materials in river water samples. Sample volumes of 50 to 60 L of river water were pumped through a 1.3 mm diameter, 200 cm high column at a rate of 7 mL/min. Desorption was carried out using a methanol/ammonia mixture (14:1) and diethyl ether.

Forty to seventy percent of the total dissolved organic carbon was isolated using the XAD-2 resins. By comparison solvent extraction of river water samples produced only 3% of the total organic carbon (citing Ogura et al., 1975), demonstrating the superiority of the XAD-2 resin method. Oxidation of the isolated compounds by potassium permangate under alkaline conditions produced aliphatic monocarboxylic acids (C_6 - C_{24}) and dicarboxylic acids (C_3-C_{11}), benzene mono-, di-,tri- and tetracarboxylic acids. The high content of aliphatic acids suggested that the source of the dissolved organic carbon was biological lipids in domestic sewage or naturally occurring phytoplankton. Palmitic acid was found to be most abundant in the hexane extracts of the oxidation products. It should be noted that the adsorption of the compounds was done at pH 2 which allowed recovery of the organic acids.

Osterroht (1974) used XAD-2 resin columns for continuous sampling of seawater. The objective of this work was to evaluate the use of XAD-2 resins for recovering non-polar organics (DDT, DDE, Aldrin and lindane pesticides; 2-chlorobiphenyl (PCB-2); n-hexadecane, pristane and phenanthrene (hydrocarbons) at concentrations ranging from 10 µg/kg to 0.01 µg/kg for the chlorinated hydrocarbons and from 100 µg/kg to 0.1 µg/kg for the hydrocarbons.

Six columns containing 390 mL of resin in total were fed with filtered sea water (spiked with the above organics) at a flowrate of 130 mL/min. Resin cleanup consisted of Soxhlet extraction with methanol. The organics were desorbed from the resin by Soxhlet extraction with methanol for 8 h. To recover the hydrocarbons, the methanol-water solvent mixture was extracted with n-hexane. The resin was then regenerated by washing with distilled water.

The recovery of the hydrocarbons from the resin was low. The filter collected most of the pristane and hexadecane as evidenced by recoveries attributed to the filter of approximately double that of the recoveries on the resin. Washing of the filter with solvent produced a 30.9% recovery for pristane, compared to 17.5% recovery from the resin. Corresponding recoveries for hexadecane were 28.7% for the filter and 15% for the resin. Total recoveries were also less than 50% for both pristane and hexadecane. For phenanthrene, a total recovery of only 34.4% was obtained, with 25.1% attributable to the resin. Better recoveries were obtained with the other compounds (except for Lindane) with over 80% being attained. The high recovery of the hydrocarbons from the filter paper was felt to be caused by the adsorption of the organic spikes onto suspended particles in the water. The suspended particles were then trapped on the filter paper, along with the hydrocarbons.

A commercially available system for sampling large volumes of water and for extraction of organics in water using XAD resins is marketed by Seastar Instruments Ltd., of British Columbia (Seastar technical bulletin, 1986). The device consists of an in-line Tefon filter holder, a pump with a flow rate capacity of 50 to 150 mL/min, and an extraction column. Extraction columns may be filled with XAD resins or other adsorbents depending on the analytical parameters of interest. For sampling of organics in water, XAD resins or C-18 bonded silica gel can be used. Volumes of up to 1000 L can be pumped from depths of 300 m. Up to 12 sampling modes are available. The unit is compact, having dimensions of 64 cm high and 14 cm diameter (without filter) and weighing 14 kg.

The sampler has been tested by the U.S. Coast Guard for its effectiveness in handling suspended materials and its suitability for use in hazardous spill response situations, where limited skilled personnel are generally used for sample collection and handling (Jadamec et al., 1986).

Pumping efficiency was found to be best at 200 mL/min and there was no decline in pump performance with the suspended material loadings encountered (actual values were not given).

The suitability of XAD resins in recovering oil and grease components in wastewaters is primarily restricted to the dissolved portion of the oil and grease (i.e. aromatic compounds). Table 19 summarizes the recoveries obtained for neutral compounds typically found in oily wastewaters (particularly hydrocarbon based). The recoveries of the aromatic compounds are generally quite good (greater than 80% under most column operating conditions. The alkanes however do not provide as good recoveries as the aromatics. However, the use of a prefilter to recover these insoluble organics may eliminate the problem and allow both differentiation of the soluble and insoluble oil fractions.

The availability of commercial systems using this method could ease the difficulties encountered in the collection and preservation of representative oil and grease containing water samples.

10.3 Suitability of Concentration and Isolation Methods for Oil and Grease Analysis

Isolation methods are more desirable than concentration methods since they have the potential benefit of in-situ extraction of oil and grease components from the water or wastewater; thereby eliminating the need to transport large volumes of water and the subsequent transportation losses. Of the isolation methods, adsorption onto sorbents preferential to non-polar solutes would provide the most suitable method for oil and grease analysis. However, only the dissolved fraction of oil and grease would be amenable to adsorption. Very little

TABLE 19. XAD-2 RESIN RECOVERIES FOR HYDROCARBONS FOUND IN PETROLEUM-TYPE WASTEWATERS

COMPOUND	RECOVERY, (%)
n-Alkanes	
Hexadecane	12[a], 3[b]
Alkylated Benzenes	
Toluene	56.5[a],100[c]
Ethyl benzene	60[a]
n-Butyl benzene	63.8[d]
Naphthalene	98[a], 100[c], 90[d], 64[f]
1-Methyl naphthalene	87[a], 90[d]
Ethyl naphthalene	64[d]
Polynuclear Aromatics	
Phenanthrene	84.3[f], 110[e]
Anthracene	83[a], 41[c], 84.3[f]
Fluorene	84[a]
Acenaphthene	92[a], 72[b]
Biphenyl	101[a], 73[c], 90[d]
Pyrene	95.7[f]
Chrysene	92.8[f]
Acenaphthalene	90[e]

Notes:
a - Schnare, 1979
b - Webb, 1975
c - Burnham, 1972
d - Stepan and Smith, 1977
e - Junk et al., 1974
f - Green and Kowalski, 1984
g - Moore and Karasek, 1984

equipment is needed for the application of adsorbents to oil and grease analysis; however, an upstream filter capable of trapping the suspended oil and grease fraction would be needed. Solvent extraction is another alternative; however, specialized equipment is needed to carry this out in the field for large sample volumes.

Of the sorbents tested for trace organics in water, XAD resins appear to provide the most flexibility with respect to desorbability and ultimate recovery of the dissolved non-polar organic solutes (compared to activated carbon and polyurethane) components in oil and grease. Compared to activated carbon, XAD resin surfaces are better defined with respect to polarity. This is reflected in the availability of XAD resins of various polarities. Thus the XAD-2 and XAD-4 resins are more likely candidates for oil and grease analysis.

Polyurethane foam may also be a good candidate for oil and grease analysis; however not as much information is available to determine its appropriateness to the analysis of oil and grease in water.

In summary, there is a wide body of information available on the use of XAD resins; and the various operating parameters and problems are well researched in the trace organics field. This data indicates that the resins would allow isolation of the dissolved components of oil and grease, in particular, the petroleum hydrocarbons. Therefore tests with XAD resins on their suitability to oil and grease analysis are warranted. The use of the XAD resins was therefore adopted in this experimental program.

Of the concentration methods, the most suitable processes that can be applied for oil and grease analysis would be a combination of membrane processes (microfiltration, ultrafiltration and reverse osmosis). The use of a two stage membrane process (e.g. microfiltration/reverse osmosis or ultrafiltration/reverse osmosis) would likely provide fractionation of the oil and grease into the dispersed and dissolved components. The method would also allow a fair size of sample to be processed, with little loss of volatile components. Therefore, further work using membranes for the analysis of oil and grease in water and wastewater is warranted.

Freeze concentration does not appear to be a widely used method and interferences by oil droplets during freezing would be expected. With evaporative methods, losses of volatile components would be expected; also, long times would be required to evaporate the sample. Therefore, evaporative methods would not be appropriate for the concentration of oil and grease containing samples.

11 EXPERIMENTAL SECTION

This section deals with the experimental details for the application of a method termed the "dual column method" for determining oil and grease at low concentrations in petroleum based wastewater. The dual column method was intended to improve upon the conventional protocol for determining oil and grease at both the sampling and quantitation stages for petroleum-based wastewaters. The method also incorporates the analysis of both suspended and dissolved components of oil and grease.

11.1 Experimental Objectives

The experimental objectives were:

(i) to evaluate the use of XAD-2 resin for adsorbing non-polar organics from a synthetic mixture and petroleum-based wastewaters.

(ii) to evaluate the use of diatomaceous earth for absorbing suspended oil components from a synthetic mixture and petroleum-based wastewaters.

(iii) to evaluate the combined use of diatomaceous earth and XAD resin to provide for complete extraction of oil and grease components from a synthetic mixture and petroleum-based wastewaters (dual column method).

(iv) to compare the dual column method with the standard partition gravimetric method for oil and grease determination in wastewater, particularly at the concentration range of interest (< 25 mg/L).

11.2 Experimental Details

The experiments were carried out in several phases. These were:

1. XAD-2 column runs with aqueous naphthalene solutions
2. Diatomaceous earth column runs with dispersions of hexadecane in water.
3. Dual column runs with a synthetic dispersions of hexadecane and naphthalene in water.
4. Dual column runs with oilfield produced water.
5. Partition-gravimetric determination of oil and grease in oilfield produced water.

Both a synthetic wastewater, representative of a petroleum based wastewater, and actual wastewaters were used. For the synthetic wastewater, a mixture of naphthalene and hexadecane, stabilized by sodium oleate was used.

Naphthalene was selected to represent a non-polar organic compound typically found in petroleum-based wastewaters. Naphthalene is also relatively soluble in water (solubility at 25°C is 31.7 mg/L as indicated in Table 3, Section 3.2.2) and would represent the dissolved fraction of oil and grease. Hexadecane was selected as a typical alkane constituent of oil and grease in a petroleum-based wastewater. It is relatively insoluble in water (solubility at 25°C is 0.9 µg/L as indicated in Table 3, Section 3.2.2) and would, therefore, represent the suspended fraction of oil and grease in the synthetic mixture and the actual wastewater.

The petroleum-based wastewater used was an oilfield produced water. This oilfield produced water is generated during the in-situ recovery of heavy oil. In the in-situ recovery of heavy oil, steam is injected into the oil formation to reduce the viscosity of the heavy oil, and thereby allow it to be pumped to the surface. The ensuing produced fluids contain oil, suspended solids and water (condensed steam and water from the oil formation). The majority of the oil and suspended solids is separated from the produced fluids through a set of unit operations (free water knockout, heat treater, desander and skim tanks) as shown in Figure 13. The water phase, known as produced water, is further treated for suspended oil and solids removal using induced gas flotation and granular media filtration. These processes remove oil and suspended solids to a level such that the produced water could be recycled for steam generation after some further polishing for hardness removal. The produced water samples used were obtained from the skim tank. To allow the use of the dual column technique, it was necessary to dilute the produced water tenfold as the concentration of the oil and grease in the sample received to bring the concentration to the range of interest.

XAD-2 resin was selected based on its well-documented ability to adsorb relatively non-polar, water-soluble organics such as those found in petroleum-based wastewaters, as discussed in Section 10.2.2.3. Since XAD-2 resins cannot effectively adsorb dispersed oil, (e.g. long chain alkanes such as hexadecane), a diatomaceous earth column was used to recover this

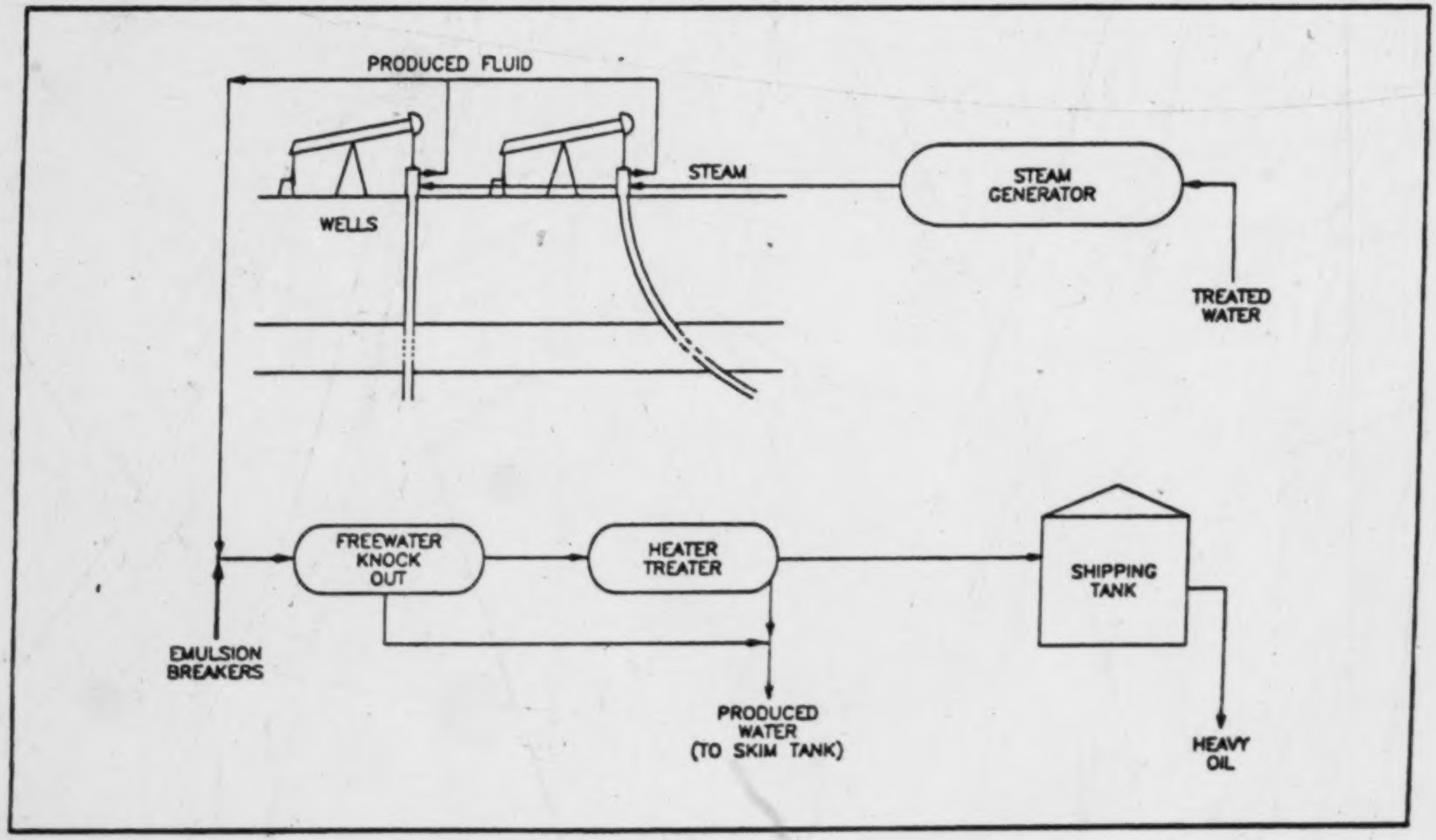

PRODUCED FLUID
WELLS
STEAM
STEAM GENERATOR
TREATED WATER
FREEWATER KNOCK OUT
HEATER TREATER
SHIPPING TANK
EMULSION BREAKERS
PRODUCED WATER (TO SKIM TANK)
HEAVY OIL

FIGURE 13: SCHEMATIC OF HEAVY OIL RECOVERY PROCESS

fraction of the oil and grease in the synthetic mixture as well as the actual wastewater.

Dichloromethane was selected as the solvent for recovering the organics from the XAD-2 resin and from the diatomaceous earth. Dichloromethane was used instead of Freon because it has been found to be a better solvent for heavier oils, as discussed in Section 7.

11.2.1 XAD-2 resin column runs

Resin column testing consisted of feeding aqueous naphthalene solutions of varying concentrations to columns of XAD-2 resins, as shown in Figure 14. Column diameter was 17 mm (i.d.). Each column was packed with resin to a height of 7 cm.

11.2.1.1 Resin cleaning. The XAD-2 resin was cleaned using two successive 24 h soxhlet extractions with 500 mL portions of dichloromethane. Resin purity was checked by taking a sample of dichloromethane which was in contact with the thimble containing the resin during the soxhlet extraction. The absorbance of this sample was tested in the UV range at 275.5 nm. Zero absorbance indicated that the resin was clean. The resin was then dried at 70°C for 1 hour, and subsequently stored in a clean glass bottle. Detailed procedures for the resin preparation step are given in Appendix A.1.1.

11.2.1.2 Detection of naphthalene. Monitoring of naphthalene was done by ultraviolet detection. Initial scanning of an aqueous solution of naphthalene indicated a strong absorbance at 275.5 nm. The instrument used was a Perkin Elmer Model 20 spectrophotometer. Cell path length used varied depending on the

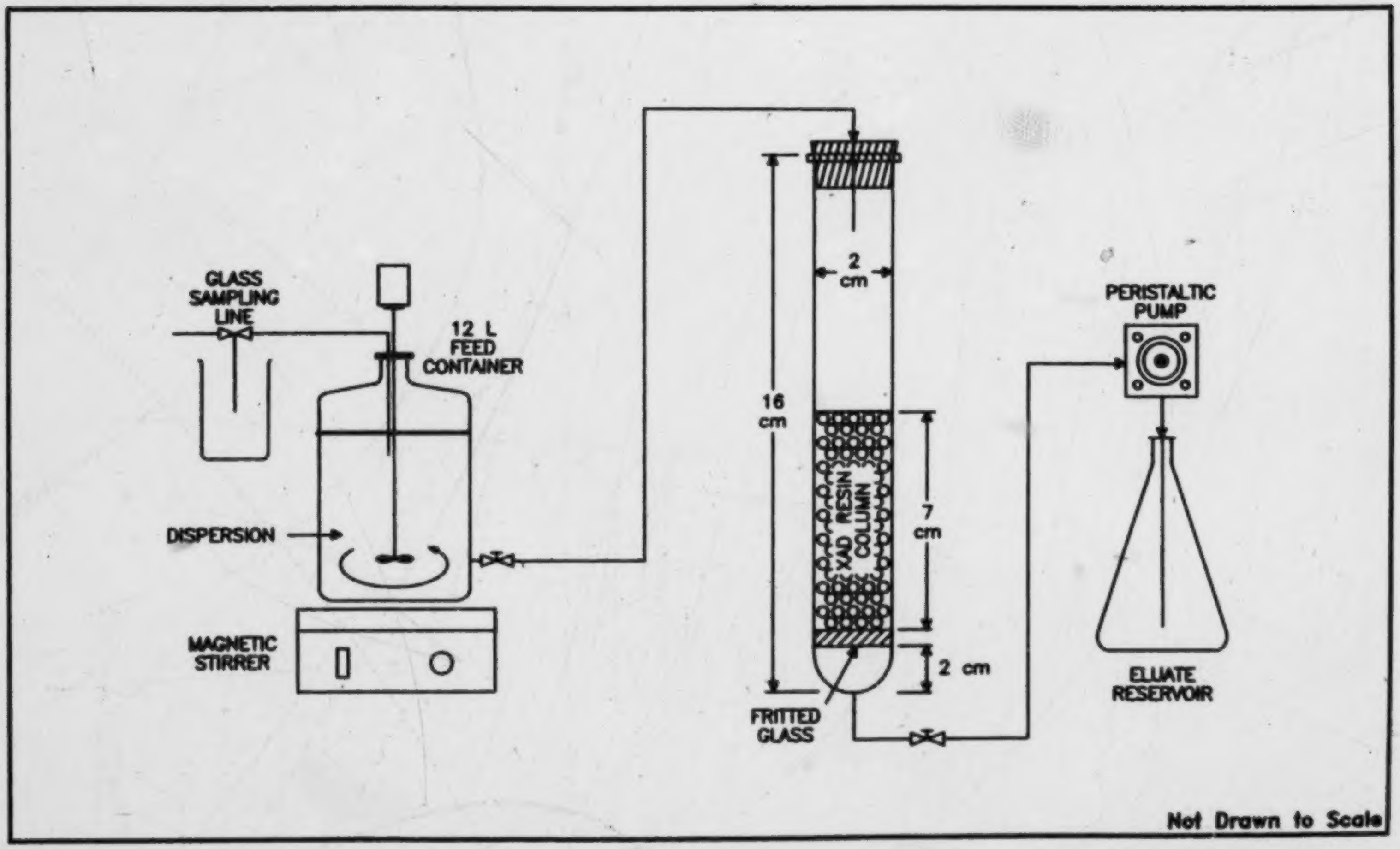

GLASS SAMPLING LINE
12 L FEED CONTAINER
DISPERSION
MAGNETIC STIRRER
16 cm
2 cm
XAD RESIN COLUMN
7 cm
2 cm
FRITTED GLASS
PERISTALTIC PUMP
ELUATE RESERVOIR
Not Drawn to Scale

FIGURE 14: XAD–2 RESIN COLUMN ASSEMBLY FOR CONCENTRATING DISSOLVED OIL AND GREASE IN WATER

expected concentration of the naphthalene in solution. At concentrations above 5 mg/L, a cell path length of 1 cm was used. Below this, a cell path length of 10 cm was used. Cell material was quartz. Detailed procedures for monitoring of naphthalene in water and solvent are found in Appendix A.1.2.

11.2.1.3 Column preparation and operation. The resin column was prepared by firstly weighing approximately 5 g of dry, clean XAD-2 resin. Methanol (30-35 ml) was then added to the resin to form a slurry which was then loaded onto the column. The methanol made the resin water-wettable, thus facilitating handling of the resin and passage of the naphthalene solution through the bed. The column was then backwashed with distilled water for approximately 20 minutes to classify the bed and also to wash it free of methanol. Following bed settling, the aqueous solution of naphthalene was fed into the bed. The effluent from the resin bed was monitored over time by withdrawing samples and monitoring the ultraviolet absorbance at regular intervals. Detailed procedures for column preparation and operation are given in Appendix A.1.3.

11.2.1.4 Column operating conditions. A 2^2 factorial design was used to allow the effect of feed flow rate and feed concentration to be determined. Midpoint experiments were run in triplicate to determine experimental error. Sequencing of the runs was random. Bed depth and operating conditions were based on manufacturer's recommendations and the published literature.

Naphthalene concentrations used were 1, 5 and 10 mg/L. Operating flow rates were 5, 10 and 20 mL/min. The final amount of naphthalene passed through the bed was kept constant at 50 mg and therefore, varying amounts of solution volumes were used to maintain this amount.

11.2.1.5 Resin desorption. After the desired volume of aqueous naphthalene solution had passed through the bed, the column was emptied and the resin was transferred to a Whatman cellulose extraction thimble (33 mm diameter X 94 mm height). The resin with the adsorbed naphthalene was then soxhlet extracted with 500 mL of dichloromethane for 24 hours (9 cycles/h). The solvent was then filtered through anhydrous sodium sulphate and analyzed by UV detection at 275.5 nm. Detailed procedures for resin desorption are given in Appendix A.1.4.

11.2.2 Diatomaceous earth column runs with dispersions of hexadecane in water

In these runs, dispersions of hexadecane in distilled water were pumped through a column of diatomaceous earth as shown in Figure 16. The concentration of hexadecane in distilled water was 5 mg/L. The absorbed hexadecane was recovered by soxhlet extraction with dichloromethane. Quantitation of the hexadecane was done using either gas chromatography or gravimetry.

11.2.2.1 Dispersion preparation. Dispersion preparation consisted of dissolving the appropriate weight of sodium oleate in a 12 L glass reservoir containing distilled water. An equivalent weight of hexadecane was weighed in a small aluminum dish, and dissolved in 1 mL of dichloromethane to facilitate its transfer and dispersion into the water. This solution was then transferred into a disposable pipette and injected into the vortex of the stirred sodium oleate solution. Detailed procedures of the dispersion preparation are given in Appendix A.2.1.

Homogeneity of the dispersion was maintained throughout the entire run by constantly mixing with a paddle type mixer at a constant speed. At the point at which the level of the dispersion was too low to facilitate mixing with the paddle mixer, a magnetic teflon stirring bar was used. The homogeneity of the dispersion was checked by withdrawing samples from 3 locations (top, middle and bottom) and measuring the turbidity, as well as by gas chromatography.

11.2.2.2 Diatomaceous earth column preparation and operation. Ten grams of diatomaceous earth were packed into a Soxhlet cellulose extraction thimble (43 mm diameter x 123 mm height). The dispersion was fed by gravity via a glass tubing into the soxhlet extraction thimble containing the diatomaceous earth. The effluent from the column was then pumped from the column via viton tubing using a Masterflex pump. The thimble was then placed in a glass container which was flanged at the middle and could be separated into two sections. Acid (50% HCl) was injected into a small mixing chamber as shown in Figure 15. The sodium oleate was thus converted to oleic acid, and hence, this also contributed to the total oil and grease of the synthetic mixture. Detailed procedures for diatomaceous earth column preparation and operation are given in Appendix A.2.2.

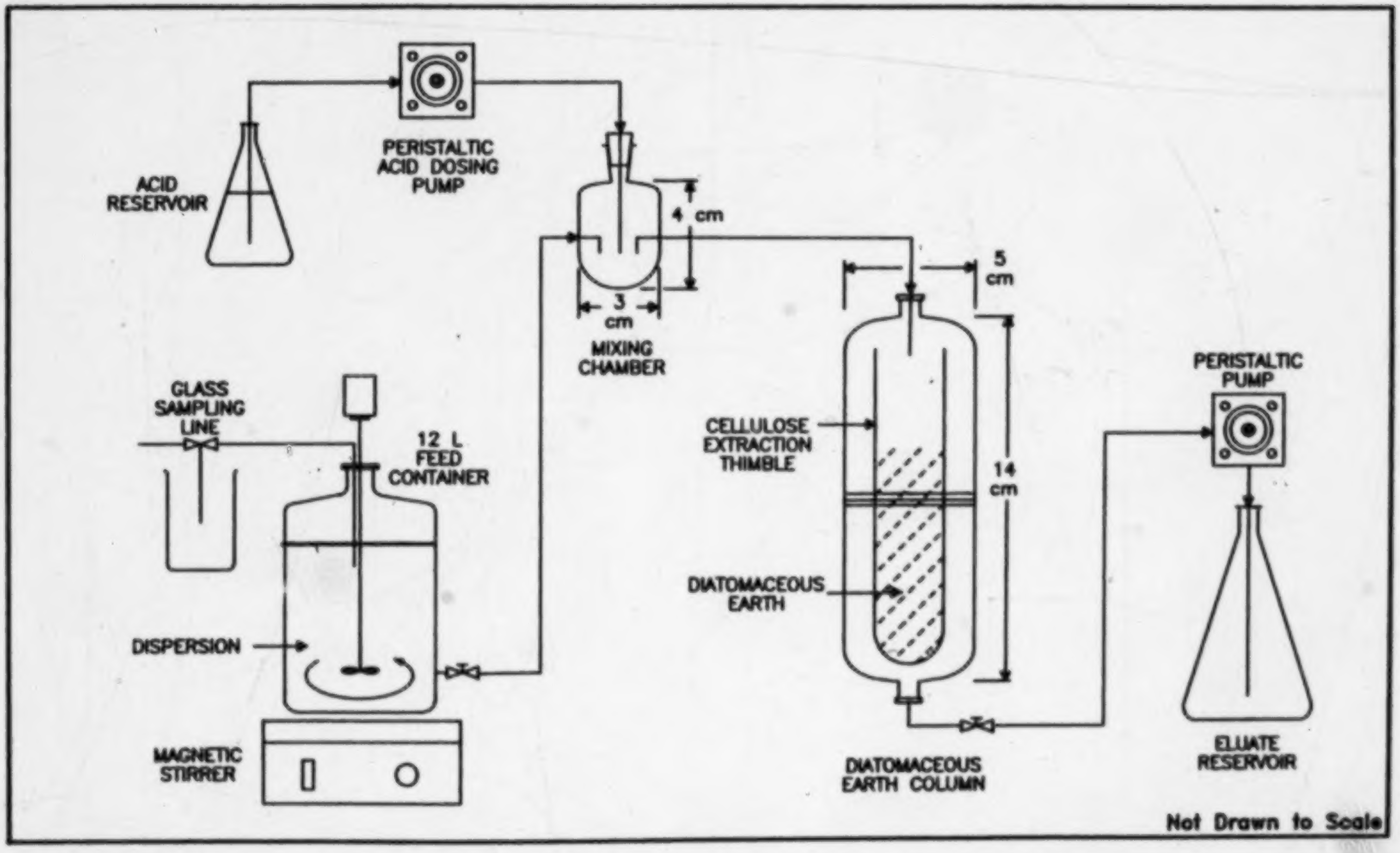

ACID RESERVOIR
PERISTALTIC ACID DOSING PUMP
4 cm
3 cm
MIXING CHAMBER
5 cm
14 cm
GLASS SAMPLING LINE
12 L FEED CONTAINER
DISPERSION
MAGNETIC STIRRER
CELLULOSE EXTRACTION THIMBLE
DIATOMACEOUS EARTH
DIATOMACEOUS EARTH COLUMN
PERISTALTIC PUMP
ELUATE RESERVOIR
Not Drawn to Scale

FIGURE 15: DIATOMACEOUS EARTH COLUMN ASSEMBLY FOR CONCENTRATING DISPERSED OIL AND GREASE IN WATER

11.2.2.3 Column operating conditions. Column operating conditions were the same as for the final selection used for the XAD resin runs, i.e. 5 mg/L hexadecane, and 5 mg/L sodium oleate, flow rate of 20 mL/min. The diatomaceous earth was Sorbacel, a Johns-Manville product, commercially used for removing fine oil from dispersions.

11.2.2.4 Recovery of hexadecane from column. After the desired volume of the dispersion of hexadecane in water had passed through the bed, the cellulose thimble was transferred directly to a soxhlet extraction assembly. The diatomaceous earth was then soxhlet extracted with 500 mL of dichloromethane for 24 hours (at 9 cycles/h). The solvent was then filtered through anhydrous sodium sulphate and analyzed by gas chromatography or gravimetry as detailed in Sections 11.2.5 and 11.2.6 respectively. Detailed procedures are given in Appendix A.2.3.

11.2.3 Sampling and analysis

Either 500 mL or 1 L samples from the main reservoir were collected using a 500 mL pipette. These samples were then extracted with dichloromethane using liquid-liquid extraction in a separatory funnel. The concentration of hexadecane was then determined using gas chromatography as detailed in Appendix A.2.4. The soxhlet extracts were also analyzed for hexadecane by gas chromatography.

11.2.4 Dual column runs with synthetic mixture of hexadecane and naphthalene

The experimental apparatus consisted of a column of diatomaceous earth followed by a column of XAD-2 polymeric resin as shown in Figure 16. A 12 L glass bottle, equipped with a paddle mixer supplied the feed to the two columns. The effluent was pumped from the columns using a Masterflex pump. Acid injection was carried out in a small mixing chamber.

In these runs, both XAD-2 resin and diatomaceous earth columns were used and an aqueous mixture of all synthetics (naphthalene, hexadecane and oleic acid) was passed through these columns. Detailed procedures for the dual column method are given in Appendix A.3

11.2.4.1 Sampling and analysis. Gas chromatography was used for determining the concentrations of hexadecane and naphthalene in the DCM extracts obtained after soxhlet extraction using similar column conditions as described in Section 11.2.4.

In another set of experiments, gravimetry was used to quantify the organic compounds recovered by the dual column method since gravimetry would be the ultimate method for quantifying the oil and grease in an actual wastewater. The solvent extracts were filtered through phase separating paper and sodium sulphate. The volume of solvent was then recorded. The DCM was then transferred to a previously weighed flask, the solvent evaporated by rotary evaporation, and the residue was weighed. Detailed procedures are given in Appendix A.3.3.

11.2.5 Dual column runs with oilfield produced water

These tests were similar to the previous runs described in Section 11.2.4 except that an actual wastewater was used. For this, two sets of oilfield produced water were used:

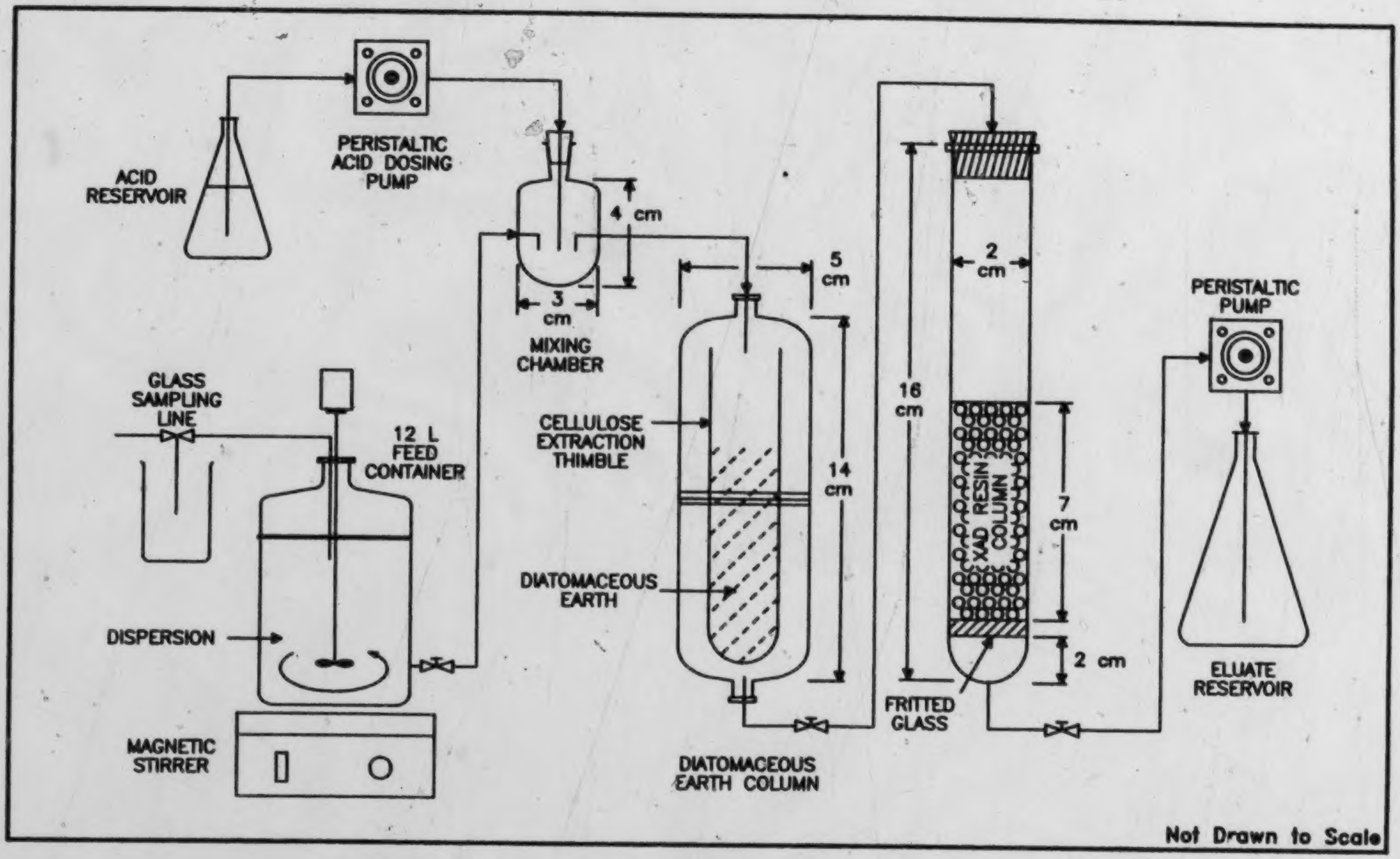

ACID RESERVOIR
PERISTALTIC ACID DOSING PUMP
4 cm
3 cm
MIXING CHAMBER
GLASS SAMPLING LINE
12 L FEED CONTAINER
DISPERSION
MAGNETIC STIRRER
5 cm
CELLULOSE EXTRACTION THIMBLE
14 cm
DIATOMACEOUS EARTH
DIATOMACEOUS EARTH COLUMN
16 cm
2 cm
XAD RESIN COLUMN
7 cm
2 cm
FRITTED GLASS
PERISTALTIC PUMP
ELUATE RESERVOIR
Not Drawn to Scale

FIGURE 16: DUAL COLUMN ASSEMBLY FOR CONCENTRATING TOTAL OIL AND GREASE IN WATER

(i) Site A and (ii) Site B. Both samples were obtained from two different heavy oil sites from Lindbergh, Alberta.

Preliminary oil and grease analysis using the partition-gravimetric analysis of the produced water indicated that the oil and grease levels were substantially above the level of interest for these experiments. Therefore, the stock sample was first filtered using a sand filter. Following this procedure, 1 litre samples were taken from this stock and then diluted to 10 litres. These diluted samples provided the feed for the experiments.

The apparatus and procedure used were the same as in Section 11.2.4 (Figure 16). Complete procedures for the dual column runs are detailed in Appendix A.4.

11.2.6 Partition-gravimetric determination of oil and grease in oilfield produced water

The standard partition-gravimetric method was used as a comparison with the dual column method. One L samples were withdrawn from the stock solutions of produced water, which was also used for the dual column method. Complete procedures are detailed in Appendix A.5.

11.2.7 Sources of errors

Quantitation of some of the sources of errors identified during these experiments were conducted. These sources of errors were as follows:

1. Column Method
    (i) DCM - soluble material leached from the phase separating paper during filtration of column solvent extracts after soxhlet extraction.

(ii) DCM soluble material leached from the diatomaceous earth and XAD resin columns during soxhlet extraction

(iii) losses caused by volatilization of components during rotary evaporation for the synthetic dispersions.

2. Partition-Gravimetric Method

   (i) DCM-soluble materials leached from the phase separating paper during filtration of the DCM after liquid-liquid extraction

   (ii) losses caused by volatilization of naphthalene during liquid-liquid extraction and rotary evaporation for the synthetic dispersions.

For 1(i), the phase separating paper was initially weighed. 300 mL of DCM used for the soxhlet extraction was poured into the filter paper. After draining off the solvent, the filter paper was then dried in an oven at 60°C for 1 h, cooled and then weighed. The difference in weights before and after passing solvent through the phase separating paper was then calculated. An average of two values were obtained, and this value was subtracted from the total weight of oil and grease obtained from the column method.

For 1(ii), 2 - 10 g quantity of diatomaceous earth were packed into 2 cellulose extraction thimbles and soxhlet extracted for 24 h with 300 mL of DCM. For the XAD resin, 2 - 5 g quantity were placed in separate cellulose extraction thimbles and were soxhlet extracted for 24 h with 250 mL of DCM. The DCM solvents were then rotary evaporated. The weight of the residue was obtained from the difference in weight between the flask before and after rotary evaporation. An average of 2 values was obtained; this was subtracted from the total weight of oil and grease obtained from the column method.

For 2(i), the values obtained from 1(i) were used. However, the weight obtained for the DCM leached materials was subtracted from the weight of oil and grease obtained from the partition-gravimetric method.

For 2(ii), 3 - 1 L samples of a 15 mg/L solution of naphthalene were extracted with 300 mL DCM in a preweighed round bottomed flask. This solution was rotary evaporated. After solvent evaporation and cooling in a dessicator, the flask was reweighed. The loss in weight was attributed to volatilization of naphthalene during liquid-liquid extraction and during rotary evaporation.

For 1 (iii), the loss caused by rotary evaporation was estimated by preparing solutions containing 45 mg each of naphthalene, hexadecane and oleic acid in DCM. Three samples were prepared and the DCM was then evaporated by rotary evaporation. The difference in weights of the empty flask and flask plus residue was obtained. The recovery was then calculated by dividing the residue weight by the orginally prepared weight of 135 mg. An average of 3 values was obtained. In another experiment, only hexadecane and oleic acid were used to prepare the solution. Therefore the difference between the recoveries obtained when only the 2 components were used compared to when all 3 components were used provided an estimate of the loss caused by volatilization of naphthalene only. Note that the losses encountered during liquid-liquid extraction and rotary evaporation are used only to qualitatively account for the difference between the original inputs and the experimentally determined weights since the variability of errors associated with such losses does not allow confidence in allowing for a constant correction factor.

12. RESULTS

12.1 XAD-2 Column Runs with Aqueous Naphthalene Solutions

The results from the XAD-2 column runs for recovering naphthalene from an aqueous solution are shown in Table 20. In these runs, an aqueous solution of naphthalene in water was pumped through the column as described in Section 11. The effects of naphthalene concentration and feed flowrate were investigated. Experiments 1,3 and 2,4 show the effect of feed concentration at a constant feed flowrate of 5 mL/min. Experiments 1,2 and 3,4 show the effect of feed flowrate at a constant concentration. Four runs at 5 mg/L and 10 mL/min allowed the determination of experimental error. An additional run using a naphthalene concentration of 4.9 mg/L and a flow rate of 20 mL/min also allowed the effect of flow rate to be determined.

Detection of naphthalene in the aqueous feed solution and the dichloromethane solvent extract obtained after soxhlet extraction was by UV adsorption at a wavelength of 275.5 nm, as previously discussed in Section 11. The plot of absorbance versus concentration was linear and the calibration equation used was: $C_{naphthalene} = 23.35 \times \text{Absorbance}$.

The plot of absorbance of naphthalene versus concentration for the dichloromethane solution was also linear in the range of interest and the calibration equation was : $C_{naphthalene} = 26.3 \times \text{Absorbance} - 1.58$.

TABLE 20. RECOVERY OF NAPHTHALENE FROM AQUEOUS SOLUTIONS USING XAD-2 RESIN

EXPT.	PREPARED NAPHTHALENE CONCENTRATION mg/L	FLOWRATE mL/min	SOLUTION VOLUME L	PERCENT NAPHTHALENE RECOVERED
1	1	5	50	103.0
2	1	20	50	98.0
3	10	5	5	98.0
4	10	20	5	93.0
5	5	10	10	98.9
6	5	10	10	98.7
7	5	10	10	98.8
8	5	10.3	20	97.9

12.2 Diatomaceous Earth Column Runs

In these runs, a dispersion of hexadecane in water (stabilized with sodium oleate) was pumped through a column of diatomaceous earth, Sorbacel (supplied by Johns-Manville, Ontario) in the apparatus shown in Figure 16.

12.2.1 Preparation of synthetic dispersion of hexadecane in water

The homogeneity of hexadecane dispersed in the water was initially checked by withdrawing samples from the top, middle and bottom sections of the reservoir in which the dispersions were prepared (for details on mode of dispersion preparation, see Section 11). The samples were analysed for turbidity. One 500 mL sample was taken at the same locations, and was extracted with 100 mL of dichloromethane and analysed for hexadecane by gas chromatography. The results of these experiments are shown in Table 21. Dispersion concentrations (hexadecane) for which both analyses (turbidity and gas chromatography) were done were 2.5 and 5 mg/L.

12.2.2 Checks on accuracy of methods.

The partition-gravimetric method may be subject to the following problems:

(i) incomplete extraction of components

(ii) losses of volatile substances during rotary evaporation

(iii) leaching of DCM soluble material from the phase separating paper

(iv) errors in weighing at low concentrations

(v) losses caused by adsorption onto glassware

TABLE 21. HOMOGENEITY OF PREPARED DISPERSIONS OF HEXADECANE IN WATER

HEXADECANE CONCENTRATION, mg/L						
prepared	measured (by GC[1])			Turbidity, ntu		
	top	middle	bottom	top	middle	bottom
2.5	1.4	1.5	1.4	2.0	2.0	2.1
5.0	3.9	3.6	3.9	2.8	3.0	2.8
20.0	11.7	12.5	11.0	---	---	---

[1] GC - gas chromatography

The diatomaceous earth column method may be subject to the following problems:

(i) losses of volatile substances during rotary evaporation

(ii) leaching of DCM soluble material from the phase separating paper

(iii) leaching of DCM soluble components from the diatomaceous earth during soxhlet extraction

(iv) losses caused by adsorption onto glassware throughout the course of the runs which lasted about 6-8 hours

(v) difficulty in maintaining stirring at the end of the run because of practical problems with the experimental setup, thereby resulting in non-homogenous conditions

Table 22 shows the magnitude of some of the errors related to the two methods; these errors have been accounted for in the results and are later presented in Table 23.

12.2.3 Determination of oil and grease concentration in synthetic dispersion of hexadecane/oleic acid in water by gravimetry

The concentration of oil and grease in the synthetic dispersion of hexadecane in water obtained using a single diatomaceous earth column method and the partition-gravimetric method is shown in Table 23. Because the dispersion was acidified just prior to entering the diatomaceous earth column, the oil and grease concentration would include the contribution by the oleic acid formed by protonation of the sodium oleate. The prepared concentration of hexadecane and sodium oleate in the dispersion fed to the diatomaceous earth column was 5 mg/L each.

TABLE 22. SOURCES OF ERRORS IN DIATOMACEOUS EARTH COLUMN METHOD AND PARTITION GRAVIMETRIC METHOD FOR DETERMINING OIL AND GREASE IN WATER

METHOD	SOURCE OF ERROR	MAGNITUDE OF ERROR, mg
Column	DCM[1]-soluble material leached from phase separating paper.	2.5
	DCM-soluble material leached from D.E.[2] column	5.0
Partition-gravimetric	DCM-soluble material leached from phase separating paper,	2.5

Notes:
[1]-dichloromethane
[2]-diatomaceous earth

TABLE 23. COMPARISON OF COLUMN METHOD WITH PARTITION-GRAVIMETRIC METHOD FOR DETERMINING HEXADECANE/OLEIC ACID CONCENTRATION IN SYNTHETIC DISPERSIONS

MEASURED CONCENTRATION,[1] mg/L		PERCENT RECOVERY[3]	
D.E.,[2] Column	Partition Gravimetric	D.E. Column	Partition Gravimetric
5.8	5.8	60.8	60.4
6.6	6.5	68.4	67.7
6.5	6.5	68.2	67.7
5.8	5.7	60.0	59.4
6.5	6.5	68.2	67.7
6.7	6.6	69.8	68.8
6.3	6.4	66.6	65.6
6.3 ± 0.2	6.3 ± 0.3	66.0 ± 2.7	65.3 ± 2.7

Notes:
[1] determined by gravimetry
[2] D.E. - diatomaceous earth
[3] based on 5 mg/L hexadecane and 4.6 mg/L oleic acid

A total of 10 L of the dispersion was prepared. A 1 L sample was withdrawn from the middle section of the dispersion using the procedure described in Section 11.2.2.1 for analysis of oil and grease by the standard partition- gravimetric method while the remaining 9 L were fed through the diatomaceous earth column.

The concentration of oil and grease obtained from the diatomaceous earth column runs was calculated by dividing the weight of the residue obtained after rotary evaporation of the dichloromethane soxhlet extract and cooling (see procedures in Section 11) by the volume of dispersion passed through the diatomaceous earth column (usually 9 L). The percent recovery was calculated by dividing the weight of oil and grease residue obtained with the column method with the amount of hexadecane and oleic acid originally used to prepare the dispersion in the 9 L volume eluted through the column. Likewise the percent recovery for the standard partition- gravimetric method was calculated by dividing the weight of oil and grease recovered in the partition-gravimetric method by the amount originally used to prepare the dispersion in the 1 L sample taken for analysis.

A student t-test ($P<0.05$) was also performed to determine whether there was a significant difference between the two methods.

12.3 Dual Column Runs

12.3.1 Determination of dispersed and dissolved oil and grease in synthetic dispersions of hexadecane/oleic acid and naphthalene by gas chromatography

The dispersed oil and grease is represented by the hexadecane in the synthetic dispersion while the dissolved oil and grease is represented by the naphthalene. Gas chromatography was used to quantify these fractions to obtain a more definite mass balance on the components since this eliminated the steps of evaporation and residue weighing in the gravimetric method. The concentrations of hexadecane and naphthalene obtained using a diatomaceous earth column followed by an XAD-2 resin column (**dual column method**) are shown in Table 24 and 25. The prepared concentration of hexadecane and sodium oleate was 5 mg/L each. The prepared concentration of naphthalene was also 5 mg/L. A total of 10 L of the dispersion was prepared. Two 1 L samples were withdrawn for analysis of oil and grease by liquid-liquid extraction (i.e. the standard partition-gravimetric method minus the solvent evaporation and residue weighing steps) while the remaining 8 L were fed through the two columns.

Quantitation of the individual components (naphthalene and hexadecane) was by gas chromatography as previously detailed in Section 11. The concentration based on the dual column run was obtained by determining the mass amount of each component recovered in the dichloromethane extract and dividing it by the volume of dispersion passed through the diatomaceous earth column (usually 8 L). The percent recovery was based on the prepared concentration of hexadecane and naphthalene (5 mg/L each) and the

TABLE 24. COMPARISON OF COLUMN METHOD WITH LIQUID/LIQUID EXTRACTION METHOD FOR DETERMINING HEXADECANE CONCENTRATION IN SYNTHETIC DISPERSIONS

MEASURED CONCENTRATION,[1] mg/L		PERCENT RECOVERY[3]	
D.E.[2] Column	LLE[4]	D.E. Column	LLE
2.4	NA	48.6	NA
1.9	NA	37.5	NA
3.9	3.8	78.2	76.0
3.0	3.6	60.8	72.0
1.9	4.1	37.3	81.2
1.6	6.1	32.1	122.0
4.3	5.4	88.5	108.0
3.0	4.4	60.2	88.0
2.5	3.4	50.5	68.0
1.7	3.8	34.0	76.0
2.2	5.0	44.8	100.0
1.7	4.7	34.7	94.0
2.6	4.5	52.0	90.0
2.2	3.1	43.6	62.0
2.7	3.2	54.9	64.0
3.2	3.6	64.9	72.0
3.3	3.6	65.7	72.0
3.7	3.6	73.1	72.0
3.3	3.7	65.8	74.0
3.2	3.5	64.5	70.0
3.4	3.2	73.0	64.0
NA	3.8	NA	76.0
3.7	4.1	78.3	82.0
4.4	4.4	88.0	88.0
3.4	NA	67.6	NA
2.9	NA	58.4	NA
4.5	NA	90.6	NA
3.0±0.3	**4.0±0.3**	**59.5±6.7**	**80.5±6.3**

Notes: [1] determined by gas chromatography, [2] D.E. - diatomaceous earth, [3] based on 5 mg/L hexadecane and corresponding volume of dispersion used, [4] liquid-liquid extraction

TABLE 25. COMPARISON OF DUAL COLUMN METHOD WITH LIQUID/LIQUID EXTRACTION METHOD FOR DETERMINING NAPHTHALENE CONCENTRATION IN SYNTHETIC DISPERSIONS

MEASURED CONCENTRATION,[1] mg/L		PERCENT RECOVERY[2]	
XAD-2 Resin Column	LLE[3]	XAD-2 Resin Column	LLE
3.9	NA[4]	77.4	NA
4.7	3.0	93.7	NA
3.5	3.2	70.5	NA
3.6	2.7	72.8	NA
4.3	2.7	85.6	NA
3.8	3.8	76.5	NA
3.9	3.6	77.1	NA
3.0	2.9	59.3	57.9
3.9	3.0	77.4	60.1
3.8	1.8	75.1	36.3
4.3	3.7	86.1	74.1
4.2	4.2	83.0	83.1
4.7	3.7	94.3	74.1
2.9	2.7	57.5	54.6
2.8	2.6	55.8	51.9
3.7	3.0	73.9	60.0
3.7	3.2	74.7	63.7
3.6	3.4	72.0	67.3
3.8	3.5	76.0	69.2
3.6	3.4	71.9	68.3
3.5	3.3	69.6	66.0
3.8	4.3	76.9	86.0
3.9	4.4	79.6	88.0
3.4	NA	69.2	NA
3.5	NA	73.8	NA
3.9	NA	79.4	NA
3.8±0.2	**3.3±0.2**	**75.3±3.5**	**66.3±5.4**

Notes:

[1] determined by gas chromatography

[2] based on 5 mg/L naphthalene of dispersion used

[3] liquid-liquid extraction

[4] not available

8 L of the aqueous dispersion passed through the column. Likewise the percent recovery for the liquid/liquid extraction method was based on an initial concentration of 5 mg/L and 1 L of sample for each component.

A student t-test ($p \leq 0.05$) was done to determine whether there was a significant difference between the two methods.

12.3.1.1 Check on accuracy of gas chromatography procedures

The recovery of each component by gas chromatography was checked by spiking column solvent extracts containing the hexadecane and naphthalene with known amounts of each compound. The difference between the concentration of the spiked solvent extracts and the unspiked solvent extract provided the concentration (and hence recovery) of the hexadecane or naphthalene by the gas chromatography analysis. Also, the reproducibility of injections was also done by sending duplicate samples for analysis. Table 26 and 27 show the recoveries for hexadecane and naphthalene respectively.

12.3.2 Determination of oil and grease concentration in synthetic dispersions of hexadecane and naphthalene concentration by gravimetry

The concentration of oil and grease in the synthetic dispersion of hexadecane, oleic acid and naphthalene obtained using the **dual column method** is shown in Table 28. The prepared concentrations of hexadecane and sodium oleate were 5 mg/L each. The prepared concentration of naphthalene was also 5 mg/L. A total of 10 L of the dispersion was prepared. One 1 L sample was withdrawn for analysis of oil and grease by the standard

TABLE 26. RECOVERY OF HEXADECANE IN GAS CHROMATOGRAPHY ANALYSIS

SAMPLE	AMOUNT OF HEXADECANE MEASURED mg			PERCENT RECOVERY OF SPIKE
	Spiked Extract[1]	Unspiked Extract[2]	Apparent Spike Recovery	
Trial 1				
DCM soxhlet extract from XAD-2 resin	9.1	0	9.1	91.0
	9.6	0	9.6	96.0
	9.9	0	9.9	99.0
	9.8	0	9.8	98.0
DCM soxhlet extract from D.E. column	10.8	0.9	9.9	99.0
	12.3	1.1	11.2	112.0
	12.7	1.1	11.6	116.0
	10.7	0.9	9.8	98.0
Trial 2				
DCM soxhlet extract from XAD-2 resin	5.3	0	5.3	106.0
	4.8	0	4.8	96.0
	5.4	0	5.4	108.0
	5.1	0	5.1	102.0
	5.2	0	5.2	104.0
DCM soxhlet extract from D.E. column	6.0	0.8	5.2	104.0
	6.1	0.7	5.4	108.0
	6.2	0.8	5.4	108.0
	6.5	0.9	5.6	112.0
	5.8	0.6	5.2	114.0

[1] DCM extract spiked with 10 mg of hexadecane in trial 1 and with 5 mg of hexadecane in trial 2

[2] DCM extract of XAD-2 column or diatomaceous earth column

Note: comparison of the means (using t-statistic at 95% confidence interval) from both trials indicate no significant difference

TABLE 27. RECOVERY OF NAPHTHALENE IN GAS CHROMATOGRAPHY ANALYSIS

SAMPLE	AMOUNT OF NAPHTHALENE MEASURED mg			PERCENT RECOVERY OF SPIKE
	Spiked Extract[1]	Unspiked Extract[2]	Apparent Spike Recovery	
Trial 1				
DCM soxhlet extract from XAD-2 resin	10.7	1.8	8.9	89.0
	11.4	1.8	9.6	96.0
	11.8	2.1	9.7	97.0
	12.3	2.4	9.9	99.0
DCM soxhlet extract from D.E. column	9.4	0	9.4	94.0
	9.8	0	9.8	98.0
	10.1	0	10.1	101.0
	8.9	0	8.9	89.0
Trial 2				
DCM soxhlet extract from XAD-2 resin	5.7	0.5	5.2	104.0
	5.0	0.5	4.5	90.0
	5.5	0.5	5.0	100.0
	5.3	0.5	4.8	96.0
	5.6	0.5	5.1	101.0
DCM soxhlet extract from D.E. column	4.9	0	4.9	98.0
	5.3	0	5.3	106.0
	5.2	0	5.2	104.0
	5.1	0	5.1	102.0
	4.9	0	4.9	98.0

[1] DCM extract spiked with 10 mg of naphthalene in trial 1 and with 5 mg of napthalene in trial 2

[2] DCM extract of XAD-2 column or diatomaceous earth column

Note: comparison of the means (using t-statistic at 95% confidence interval) from both trials indicate no significant difference

TABLE 28. COMPARISON OF DUAL COLUMN METHOD WITH PARTITION-GRAVIMETRIC METHOD FOR DETERMINING OIL AND GREASE IN SYNTHETIC DISPERSIONS

OIL AND GREASE CONCENTRATION, mg/L

Dual Column Method			Partition Gravimetric
Diatomaceous Earth Column	XAD-2 Resin Column	Combined Columns	
7.4	7.4	14.8	7.5
6.6	6.8	13.4	8.8
6.5	6.0	12.6	9.3
6.3	6.1	12.4	8.6
5.9	6.6	12.5	6.7
7.5	6.7	14.6	9.8
7.5	5.6	13.4	9.9
8.7	7.4	16.4	7.5
6.4	7.1	13.8	8.8
6.5	6.6	13.1	7.4
6.0	6.8	12.7	8.8
4.7	7.0	11.7	9.9
6.6	5.7	12.2	13.1
5.8	6.6	12.4	7.9
4.4	6.8	11.2	NA
5.9	7.9	13.9	NA
6.4±0.5	**6.7±0.3**	**13.2±0.6**	**8.9±0.8**

partition-gravimetric method while the remaining 9 L were fed through the two columns.

The oil and grease concentration based on the dual column run was obtained by totalling the weight of the residues obtained after rotary evaporation of the dichloromethane soxhlet extracts from both columns (see procedures in Section 11) and dividing this weight by the volume of dispersion passed through the columns (9 L).

The dispersed oil and grease was considered to be that recovered on the diatomaceous earth column. The dissolved oil and grease was considered to be that portion recovered on the XAD-2 resin column.

A student t-test ($P \leq 0.05$) was done to determine whether there was a significant difference between the two methods.

12.4 Dual Column Runs with Oilfield Produced Water

The results of experiments conducted with actual wastewater, two oilfield produced water samples, are shown in Tables 29 and 30. Preliminary determination of the oil and grease concentrations (using the partition-gravimetric method) of the produced water samples as received indicated concentrations of 30 and 100 mg/L, which were higher than desired. Therefore the produced waters were diluted ten- fold to bring the concentration to the level of interest.

The experiments were conducted in accordance with the procedures detailed in Section 11. Two 1 L samples were taken

TABLE 29. COMPARISON OF OIL AND GREASE CONCENTRATION USING DUAL COLUMN METHOD AND PARTITION-GRAVIMETRIC METHOD FOR AN OILFIELD PRODUCED WATER FROM SITE A

OIL AND GREASE CONCENTRATION, mg/L			
Dual Column Method	Partition Gravimetric	Dispersed (DE column)	Dissolved (XAD-2 column)
12.0	11.5	8.0	3.4
12.9	10.7	8.7	2.5
12.0	11.8	9.7	2.6
14.5	11.7	10.9	3.5
13.7	11.4	10.5	3.2
13.6	11.3	10.5	3.1
15.9	11.8	12.7	3.2
13.2±1.3	11.5±0.3	10.1±1.1	3.1±0.3

TABLE 30. COMPARISON OF OIL AND GREASE CONCENTRATION USING DUAL COLUMN METHOD AND PARTITION-GRAVIMETRIC METHOD FOR AN OILFIELD PRODUCED WATER FROM SITE B

OIL AND GREASE CONCENTRATION mg/L		OIL AND GREASE RECOVERED, mg
Dual Column	Partition-Gravimetric	XAD-2 Resin Column
1.9	1.3	15.3
2.5	1.3	21.9
2.5	ND[3]	20.1
2.4	ND	19.5
3.7	ND	29.2
2.3	ND	18.6
2.6	ND	20.8
2.5	ND	19.9
2.5	ND	19.7
2.6±0.3		**20.6±2.4**

Notes:

[1] Generally, no dispersed oil and grease was obtained with this sample.

[2] Volume of produced water eluted through columns was 8 L.

[3] ND - non-detectable

for oil and grease analysis using the partition-gravimetric method while the remaining 8 L were eluted through the dual columns of diatomaceous earth and XAD resin.

13 DISCUSSION

Tables 20 to 30 present the results of all the experiments conducted. The main results (mean values) are expressed in terms of a 95% confidence interval.

13.1 XAD-2 Column Runs with Aqueous Naphthalene Solutions

Good recoveries of naphthalene from the XAD-2 column runs were obtained, as shown in Table 20. The percent recovery of naphthalene ranged from 97.9% to 103%. The main objective of these runs was to determine the effects of flowrate and feed concentration on the recovery of naphthalene using the XAD column so that operating conditions for subsequent runs with both XAD-2 resin and diatomaceous earth columns could be established. The results of these tests indicated that the effect of increasing flowrate from 5 mL/min to 20 mL/min on the recovery of naphthalene was negligible (98% and 103% respectively at concentration of 1 mg/L). Similarly, at a concentration of 10 mg/L, and flow rates of 5 and 20 mL/min, there was little difference in napthalene recovery (98% and 93% respectively).

The experimental error was insignificant based on the results of the four midpoint runs (5 mg/L and 10 ml/min.), as shown in Table 20. The naphthalene recoveries ranged from 97.9 to 98.9% for these four runs.

The results of the XAD-2 resin column runs showed that good recoveries could be achieved at 2[illegible] mL/min and that operating at a reduced flowrate would lengthen the run time substantially. Operating at 20 mL/min. was judged to be more practical.

13.2 Diatomaceous Earth Column Runs

13.2.1 Preparation of Dispersion of Hexadecane in Water

From Table 21, the method of preparing the dispersion of hexadecane in water was reasonably good, as gauged by the closeness in values of the concentration of hexadecane. Gas chromatography measurements indicated a value of 1.4 mg/L, 1.5 mg/L and 1.4 mg/L for samples withdrawn from the top, middle and bottom locations of the reservoir in which the dispersion was prepared. However, the concentration of hexadecane was found to be only 58%, 76% and 59% of the prepared concentration of hexadecane (2.5, 5 and 20 mg/L respectively). The difference between the two concentrations could be attributed to losses caused by adsorption of hexadecane onto the walls of the 12 L glass reservoir containing the dispersion. The amount of hexadecane adhering to the sides of the glass reservoir was not quantified since there was difficulty in rinsing the container with solvent because of its large volume (16 L).

Turbidity was also used to determine the homogeneity of the dispersion prepared. The turbidity values were quite similar for all locations, confirming the results of the gas chromatography analysis. However, because of the losses associated with adsorption of the hexadecane on the walls of the reservoir, it was concluded that turbidity could not be used as an absolute measure of hexadecane concentration. Therefore, the use of turbidity during these experiments was limited to only measuring the effluent from the diatomaceous earth column, to get an idea of whether substantial leakage of hexadecane was occurring.

13.2.2 Sources of errors

Table 22 shows the magnitude of the sources of errors identified for the column method and the partition-gravimetric method. These errors have been accounted for as previously discussed in Section 11.2.7.

13.2.3 Comparison of partition-gravimetric method and diatomaceous earth column runs for determining oil and grease in synthetic dispersion

As shown in Table 23, the diatomaceous earth column method yielded an average oil and grease concentration of 6.3±0.2 mg/L while the value obtained using the partition-gravimetric method was 6.3±0.3 mg/L. These oil and grease concentrations were based on a total of seven experiments. In these runs, both hexadecane and oleic acid are measured, since the sample was acidified. There was clearly no difference between the two methods.

The main source of error for the diatomaceous earth column method was the contribution by DCM-soluble materials leached from the diatomaceous earth which amounted to an average of 5 mg. An average of 2.5 mg of DCM-soluble material was leached from the phase separating paper used to filter the solvent. For the partition-gravimetric method the main error was also due to the DCM soluble material leached from the phase separating paper.

The weight of oil and grease recovered from the diatomaceous earth column averaged 57.0±2.4 mg for 7 runs. This weight accounted for 66.0±2.7% of the original amount of oil and grease fed to the diatomaceous earth column. Considering the length of time of the run, and the losses caused by adsorption, this recovery was quite good. The recovery of oil and grease using the partition- gravimetric method was 65.3±2.7% which is of the same order as for the diatomaceous earth method. Adsorption losses onto the glassware was considerable since only 66% of the total oil and grease used to prepare the dispersion could be accounted for.

The methods therefore appear to be quite similar for a single component in water with respect to accuracy (i.e. recovery) and precision (reproducibility). However, the diatomaceous earth column method would facilitate sampling and handling losses as previously discussed in Section 6; thus providing additional benefits compared to the partition-gravimetric method which relies on proper sampling and little sample losses for good accuracy.

13.3 Dual Column Runs - Comparison of Column Concentration Method and Liquid/Liquid Extraction Method for Determining Oil and Grease in Synthetic Dispersion

13.3.1 Quantitation by gas chromatography

13.3.1.1 Dispersed oil and grease. As shown in Table 24, the concentration of hexadecane obtained using the diatomaceous earth column to concentrate the dispersed oil and grease fraction of the synthetic dispersion was 3.0±0.3 mg/L, based on a total of 26 runs. The hexadecane concentration obtained using liquid-liquid extraction was 4.0±0.3 mg/L, based on a total of 22 runs. Based upon a t-test, the two methods were significantly different ($P<0.5$).

The variability with the column concentration method was much higher than the liquid-liquid extraction method; as indicated by the sample relative standard deviations which were 30% and 18% respectively. Therefore it was concluded that the liquid-liquid extraction method provided better precision than the column method. The accuracy of the liquid-liquid extraction method was also better, as reflected by the higher recovery (80.5±6.7%) compared to the column method (recovery = 59.5±6.3%).

The amount of hexadecane recovered on the XAD-2 resin was found to be non-detectable in most cases.

The percentage of the original weight of hexadecane fed to the diatomaceous earth column recovered was 61.2±7.9%. While some losses occurred on the XAD-2 column (approximately 2.5%), this was considered to be negligible. The majority of losses was likely due to adsorption of the hexadecane onto the walls of the glass reservoir and the tubings. Occasionally, liquid-liquid extractions of the eluates from the diatomaceous earth runs were done, and the extracts analysed by gas chromatography. However, no hexadecane was found in these eluates, indicating that the diatomaceous earth column was effective in trapping the hexadecane oil particles.

The percent recovery ~~of~~ the amount of hexadecane used to prepare the dispersion is similar to that (66.0±1.6%) obtained in the runs where quantitation was by gravimetry (Section

13.2.2). This supports the argument that the losses are primarily due to adsorption.

13.3.1.2 Dissolved oil and grease. As shown in Table 25, the concentration of naphthalene obtained using the XAD column concentration method was 3.8±0.2 mg/L. The concentration obtained using liquid-liquid extraction was 3.3±0.2 mg/L. Based upon a t-test, the two methods were significantly different ($P<0.5$).

The relative standard deviations were 13% for the XAD-2 column method and 15% for the liquid-liquid extraction method, indicating that the former method was slightly more reproducible. The accuracy of the XAD-2 column method appeared to be better since the recovery of naphthalene averaged 75.3±3.5% compared to 66.3±5.4% for the liquid-liquid extraction method.

For these experiments, the amount of naphthalene recovered on the diatomaceous earth was non-detectable in most cases. The recovery of naphthalene in the gas chromatography analysis averaged 100% as shown in Table 27. Therefore, losses of naphthalene could have occurred because of volatilization of naphthalene from the reservoir over the 6-7 hour run and by adsorption onto the glass container walls. However, these losses could not be quantified.

Delays in analysing the samples by gas chromatography may have introduced errors in the above data. Delays of up to 1 - 2 months were experienced, as well as machine malfunctions. The gas chromatography column was not strictly devoted to the analysis of the components in these experiments; and hence some interferences may have occurred. At best, recovery checks using spiked samples of hexadecane and naphthalene were conducted; although not with all batches of samples submitted. A total of about 6 batches of samples were submitted; of which recovery checks for two batches were made. Therefore these factors would account for the high variability in the values obtained in the above results.

13.3.2 Quantitation by gravimetry

Quantitation by gravimetry introduced additional steps compared to quantitation by gas chromatography. For both the partition-gravimetric method and the dual column method, the additional steps were: evaporation of the soxhlet solvent extracts, cooling and weighing of the distilling flasks containing the residues. For the partition-gravimetric method, losses of volatiles during liquid liquid extraction would also be a source of error. The errors involved would therefore relate to: losses of volatiles during rotary evaporation and errors in weighing. The magnitude of all the sources of errors for the two methods was previously shown in Table 22 except for that caused by the losses of volatiles. Errors in weighing cannot be accounted for.

As previously discussed in Section 13.3.1, DCM-soluble leached material from the phase separating paper used to assist in removing water from the solvent extracts contributed a source of error for both methods. Also, in the dual column method, there were additional contributions to the final weight of the residue by DCM soluble materials leached from the column media (diatomaceous earth and XAD resin) during soxhlet extraction.

The contribution of these errors could be significant depending on the method used. For the partition-gravimetric method, losses caused by volatilization of naphthalene during liquid-liquid extraction could be as high as 19.1% (average of 18, 17.3 and 22%). Contributions to the final weight by DCM soluble material leached from the phase separating paper averaged 2.4 mg. Losses occurring during rotary evaporation were found to be negligible (approximately 4% of the final weight recovered).

For the dual column method, the contribution of DCM soluble materials by the diatomaceous earth was 5.0 mg. The contribution of DCM soluble materials leached from the XAD-2 resin during soxhlet extraction was estimated at 0.5 mg. The overall contribution of these additional weights (including 2.5 mg from the phase separating paper) assuming an input of 15 mg/L of oil and grease would therefore amount to 1.- 0.8 mg/L for the volume (8 - 10 L) used in these experiments. This would represent a 7 - 5% error in the final value obtained for the total oil and grease for the dual column method. By comparison, for the partition-gravimetric method, the error caused by volatilization during liquid liquid extraction would be substantially higher (19.1%). The contribution of DCM leached materials from the phase separating paper would also be substantial to the final oil and grease value obtained by the partition-gravimetric method.

As shown in Table 28, the total oil and grease concentration obtained using the dual column method was 13.2±0.6 mg/L, compared to 8.9±0.8 mg/L using the partition-gravimetric method (based on a total of 14 runs). Based upon a t-test, the two methods were significantly different ($P<0.5$).

Comparison of the relative standard deviations for the both methods indicated that the partition-gravimetric method was less reproducible than the column concentration method (17% for the partition-gravimetric method compared to 10% for the dual column method). (In these runs using gravimetry for quantitation, the reproducibility was much better for both methods than when gas chromatography was used.) The recovery of the original weight of oil and grease components recovered in the dual column method was 88.1±5.1%. By comparison, the percentage of oil and grease recovered by the partition-gravimetric method was 60.7±5.5%. Therefore the dual column method was more accurate than the partition-gravimetric method when using gravimetry as the mode of quantitation.

13.3.2.1 Dispersed oil and grease. Also shown in Table 28 is the contribution of the total oil and grease by the dispersed fraction (hexadecane and oleic acid combined). The concentration of the dispersed oil and grease obtained from the diatomaceous earth column method was 6.4±0.5 mg/L. The percent recovery (assuming the dispersed oil and grease to consist of both hexadecane and oleic acid) was 60.7±5.5%. This value is similar to that obtained previously in single column runs (Section 13.2.2).

13.3.2.2 Dissolved oil and grease. As shown in Table 28, the contribution of the total oil and grease by the dissolved fraction (naphthalene) using the XAD column concentration method was 6.7±0.3 mg/L. The amount of the dissolved fraction obtained was considerably higher than the amount which was fed as naphthalene (5 mg/L). However, there would be a contribution by oleic acid which represented 1/3 of the oil and grease in the synthetic mixture (after acidification). This would therefore account for the increased amount of dissolved oil and grease in this solvent fraction. Tests were not conducted to see the amount of oleic acid that would have adsorbed onto the XAD resin; however, results of researchers (Junk, 1975) would indicate good recoveries of oleic acid. Additional capture of hexadecane onto the XAD resin would be expected to be negligible as the previous tests using gas chromatography for quantitation indicated.

The reproducibility of the XAD-2 resin column method in recovering the dissolved oil and grease fraction was also quite good as reflected by the relative standard deviation of 9%. It was not possible to deduce the accuracy (i.e. recovery) of the XAD-2 column part of the method because of the contribution by the oleic acid.

The amount of oil and grease recovered by the diatomaceous earth column was 56.5±3.5 mg, while that recovered with the XAD-2 resin column was 61.1±3.7 mg. By contrast, the amount recovered by the partition-gravimetric method was 8.9±0.8 mg. The percent recovery by the partition-gravimetric method was substantially less than the dual column method (60.7±5.5%

compared to 88.1±5.1%for the dual column method). Therefore, the dual column method was able to concentrate the oil and grease substantially above that of the partition-gravimetric method and also allowed better recoveries.

13.4 Produced Water Samples

As shown in Table 29, the oil and grease concentration obtained by the dual column method was 13.2±1.3 mg/L for the produced water sample from Site A. The corresponding value for the partition- gravimetric method was somewhat lower at 11.5±0.3 mg/L. Based upon a t-test, the two methods were significantly different ($P<0.5$).

Both methods had good reproducibility. The partition-gravimetric method was more reproducible than the dual column method since the percent standard deviation was 4% compared to 11% for the latter method. The accuracy of the methods cannot be determined since the true value of the oil and grease concentration is not known. Therefore, precision is the only tangible way of comparing the methods. The results obtained in these runs were similar to the runs using synthetic dispersions of hexadecane in water (Section 12). Therefore, the dual column method could be used directly at the point of sampling to overcome the sampling difficulties already mentioned previously.

The breakdown of the total oil and grease concentration into its component dispersed and dissolved oil and grease is also shown in Table 29. The dispersed oil and grease concentration obtained for the Site A produced water was 10.1±1.1

mg/L. The dissolved oil and grease concentration averaged 3.1±0.3 mg/L. The relative standard deviation for the dispersed oil and grease was 15% while that for the dissolved oil and grease concentration was 13%.

For runs where the same volume (8 L) of produced water was eluted through the columns, the mass amount (i.e. weight of oil and grease) obtained for the amount of dispersed oil ranged from 76.6 - 102.5 mg. The mass amount of dissolved oil and grease was generally constant (range: 20.1 - 24.6 mg), as would be expected. The partition-gravimetric method gave quite reproducible mass amounts ranging from 10.7 - 11.8 mg.

As shown in Table 30, for the Site B produced water sample, only the dual column method could be applied. After correcting for the sources of errors, the oil and grease concentrations were found to be negative for the partition gravimetric method. The concentration of oil and grease obtained by the dual column method was 2.6±0.3 mg/L. All the accountable oil and grease (20.6±2.4 mg) was obtained on the XAD-2 column only.

14 CONCLUSIONS AND RECOMMENDATIONS

14.1 Conclusions

Based on the experimental results, the following is concluded:

1. Homogeneous synthetic dispersions of oil in water, as represented in these experiments by hexadecane, sodium oleate and naphthalene, could be successfully prepared using high speed mixing.
2. Losses ranging from 20 - 42% of the known amount of components used to prepare synthetic dispersions were obtained. These losses were presumed to be caused by adsorption onto the surfaces of the apparatus.
3. Good recoveries of naphthalene from synthetic solutions, by adsorption on XAD-2 resin followed by desorption using dichloromethane, were obtained. Recoveries ranged from 93% to 103% for flowrates ranging from 5 mL/min to 20 mL/min.
4. Gravimetric determination of dispersed oil and grease using a diatomaceous earth column and the standard partition-gravimetric method indicated that both methods were similar for synthetic dispersions of hexadecane/oleic acid in water at a total concentration of 9.6 mg/L.
5. Quantitation using gas chromatography allowed more specific tracing of the effectiveness of the dual column method and the liquid-liquid extraction part of the partition-gravimetric method for the synthetic dispersions of hexadecane and naphthalene. A significant difference was

observed between both methods. The liquid-liquid extraction method produced more reproducible results, as well as slightly higher recoveries for the dispersed oil, i.e. hexadecane. For the dissolved fraction, the XAD-2 column method was slightly better both with respect to precision and accuracy.

6. Quantitation using gravimetry when the dual column method was used for the synthetic dispersions of hexadecane and naphthalene indicated that the dual column method produced more reproducible and more accurate results than the partition-gravimetric method.
7. The dual column method was able to provide a breakdown between the dispersed oil and grease and the dissolved oil and grease. For the synthetic mixture, the concentration of the dispersed oil and grease was 6.4±0.5 mg/L. The concentration of dissolved oil and grease was 6.7±0.3 mg/L.
8. The dual column method allowed quantitation of samples having concentrations below the detection limit of the partition-gravimetric method (<25 mg/L).
9. For an oilfield produced water from Site A, the partition-gravimetric method produced slightly better reproducible results than the dual column method for an estimated concentration of oil and grease of about 15 mg/L. The relative standard deviations were 4% and 11% for the partition-gravimetric method and the dual column method respectively. However, the dual column method would still provide significant advantages to the partition-gravimetric

method for such samples by (i) allowing sample collection over a longer time period, (ii) eliminating sample losses from field to lab, (iii) reducing the tedium of liquid-liquid extraction using a separatory funnel and (iv) allowing a greater confidence in weight measurements.

10. The dual column method was able to provide a breakdown between the dispersed and dissolved oil and grease concentration. For the produced water from Site A, the dispersed oil and grease concentration was 10.1±1.1 mg/L, while the dissolved oil and grease concentration was 3.1±0.3 mg/L. For the produced water from Site B, the oil and grease in the sample consisted of only dissolved oil and grease at a low concentration. The partition-gravimetric method could not detect to the levels of oil and grease in this sample. The dual column method allowed detection of dissolved oil and grease concentration, which was at a level of 2.6±0.3 mg/L.

11. The main sources of errors in both methods were caused by dichloromethane soluble components that had been leached from the materials (diatomaceous earth, XAD-2 resin and phase separating paper) used in these experiments. The contribution of the relevant errors was greater in the partition-gravimetric method than for the dual column method because of the larger mass amounts of target material which could be obtained in the dual column method.

12. In general, the results of the experimental work demonstrates that the dual column method could provide

substantial advantages over the standard partition-gravimetric method. The main advantages would be in the on-site sampling of large volumes of oily wastewaters containing low concentrations of oil and grease (<25 mg/L), and the ability to distinguish between dissolved and dispersed oil and grease. For the very low concentrations of oil and grease (less than 5 mg/L), which are apt to be dissolved oil and grease, the method would superior to that of the partition-gravimetric method. In addition, proper process evaluation of oil removal processes would be possible since a direct measure of the suspended oil would be achievable by the method.

14.2. Recommendations

Therefore, refinements to the dual column method should consist of:

(i) a pretreatment of the diatomaceous earth by solvent washing, and drying to eliminate the leaching of solvent soluble components from the diatomaceous earth

(ii) elimination of the use of phase separating paper for separating the solvent and water.

(iii) testing at higher flowrates (> 20 mL/min) to allow shorter times for sampling

(iv) construction of a more durable column set-up (e.g. use of teflon columns).

(v) field testing of the dual column method.

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APPENDIX A

A.1 XAD-2 RESIN COLUMN RUNS

A.1.1 Resin Cleaning

Materials: XAD-2 resin (Rohm and Haas, supplied by BDH Chemical), dichloromethane (99.8% purity, max. UV cutoff: 233 nm, supplied by Caledon Laboratories), cellulose extraction thimble (Whatman, 33 mm diameter X 94 mm height), soxhlet extraction assembly, heater, measuring cylinder, UV- spectrophotometer (Perkin Elmer Model 20 or equivalent), quartz cuvette, pipette, drying oven.

Procedure

1. Transfer about 50 g of XAD-2 resin into a cellullose extraction thimble.
2. Add 500 mL of dichloromethane to distilling flask.
3. Soxhlet extract for 2 - 24 hour periods, changing the solvent after 24 hours.
4. Pipette 5 mL of dichloromethane into a quartz cuvette (cell path length of 1 cm).
5. Obtain absorbance of the dichloromethane following procedure in Appendix A.1.2.
6. Record absorbance at 275.5 nm. If absorbance is zero, then the resin is clean. If not, repeat soxhlet extraction with more solvent.
7. Dry resin at dried at 70°C for 1 hour to drive off solvent.
8. Store in a clean glass bottle.

A.1.2 Determination of Naphthalene by Ultraviolet Spectrophotometry

Preparation of Calibration Standard Solutions

Materials: Naphthalene, organic free distilled water, 1 L volumetric flask, 100 mL volumetric flasks, magnetic plate and stirrer, squeeze bottle, analytical balance, plastic weighing dish, spatula.

Procedure

1. Weigh 20 mg of naphthalene in a tared weighing dish
2. Transfer to 1 L volumetric flask containing organic-free distilled water
3. Add organic-free distilled water to bring level to 1 L mark
4. Stir with a magnetic stirrer until all the naphthalene dissolves, usually overnight.
5. Prepare solutions corresponding to 1, 2, 5, 10, 15 and 20 mg/L by serial dilution.

Calibration of UV spectrophotometer

Materials: double beam UV-spectrophotometer (Perkin Elmer Model 20 or equivalent), deuterium lamp, quartz cuvettes (1 cm and 10 cm path lengths (Suprasil or equivalent)), pipette, standard aqueous naphthalene solutions, Kimwipe tissues.

Procedure

1. Switch on UV spectrophotometer, allow to warm up according to manufacturer's specified time. Ensure deuterium lamp is being used.
2. Set slit width setting to 1.
3. Set absorbance wavelength at 275.5 nm.
4. Pipette 5 mL of distilled water into cuvette.

5. Wipe cuvette with Kimwipe tissue.
6. Transfer cuvette (holding carefully at the top of cuvette) to reference holder of UV spectrophotometer.
7. Rinse a second cuvette with a few mLs of the standard naphthalene solution. (Start with most dilute solution). Discard solution.
8. Pipette 5 mL of same naphthalene solution into the cuvette, taking precautions to wipe the cuvette and to hold with a Kimwipe and to hold carefully at the top edges.
9. Insert cuvette into sample holder of spectrophotometer.
10. Record absorbance value for standard solution
11. Repeat steps 6 to 10 for remaining standard solutions.
12. Plot absorbance vs concentration on squared paper.

Determination of naphthalene concentrations

1. Insert sample into cuvette taking precautions to wipe the cuvette clean.
2. For concentrations above 5 mg/l, use the cuvette with the cell path length of 1 cm. For concentrations below 5 mg/L, use the cuvette with a cell path length of 10 cm.
3. Determine concentration of naphthalene from calibration curve.

A.1.3 XAD-2 Column Preparation and Operation

Solution Preparation

Materials: Naphthalene (Baker analyzed), distilled water, 12 L glass reservoir, paddle mixer and electric motor, analytical balance, plastic weighing dish, spatula.

Procedure:

1. Weigh desired amount of naphthalene in a tared weighing dish
2. Transfer to 12 L glass reservoir containing distilled water
3. Stir with a electric paddle mixer until all the naphthalene dissolves, usually overnight.
   (Note: cover reservoir with aluminum foil to prevent losses of naphthalene by volatilization.)

Column Preparation

Materials: cleaned and dried XAD-2 resin (Rohm and Haas supplied by BDH Chemicals), glass column (17 mm i.d. X 200 mm height) with fritted base (see Figure A.1), distilled water, methanol, 100 mL beaker, weighing dishes, spatula, analytical balance.

Procedure

1. Weigh 5 g of dry, clean resin in a tared 50 mL glass beaker.
2. Add 30-35 mL of methanol to the resin
3. Stir XAD-2 resin and methanol to form a slurry.
4. Pour XAD-2 resin slurry into the column.
5. Backwash column with distilled water for approximately 20 minutes to classify the bed and also to wash it free of methanol. Allow fines to wash over.
6. Allow resin to settle. Column is now ready for use.

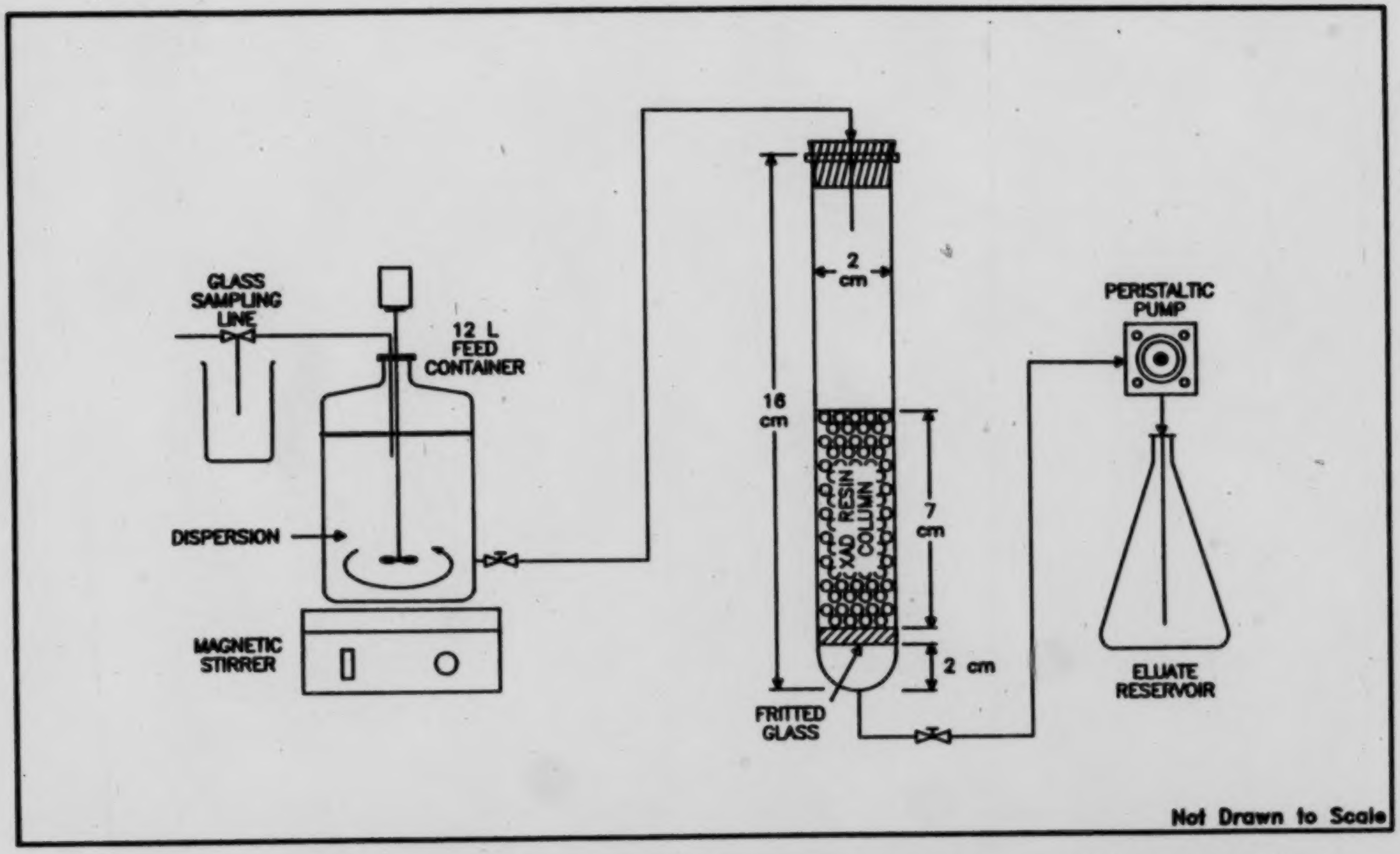
GLASS SAMPLING LINE
12 L FEED CONTAINER
DISPERSION
MAGNETIC STIRRER
16 cm
2 cm
XAD RESIN COLUMN
7 cm
2 cm
FRITTED GLASS
PERISTALTIC PUMP
ELUATE RESERVOIR
Not Drawn to Scale

FIGURE A.1: XAD–2 RESIN COLUMN ASSEMBLY FOR CONCENTRATING DISSOLVED OIL AND GREASE IN WATER

Column Operation

Materials: glass reservoir with aqueous naphthalene solution, prepared XAD-2 resin column, connecting glass or teflon tubing, masterflex pump, Viton tubing, collection vessel (4 L erlenmeyer flask), UV-spectrophotometer (Perkin-Elmer Model 20 or equivalent), quartz cuvettes (cell path length of 10 cm).

Procedure

1. Connect glass column outlet to Masterflex pump inlet using Viton tubing.
2. Connect reservoir outlet to inlet of glass column (see Figure A.2).
3. Open valve feeding the XAD-2 column.
4. Open glass column outlet valve.
5. Set pump at desired flow rate.
6. Switch on pump.
7. Adjust pump flow rate as needed
8. Monitor the effluent from the resin bed occasionally. Withdraw a 5 mL sample every hour to determine whether there is leakage of naphthalene from the XAD column. Transfer 5 mL sample to a quartz cuvette and measure the UV absorbance as in Appendix A.1.2.
9. Allow naphthalene solution to feed through the XAD-2 column.
10. Switch off pump when all the solution has been pumped through the column.

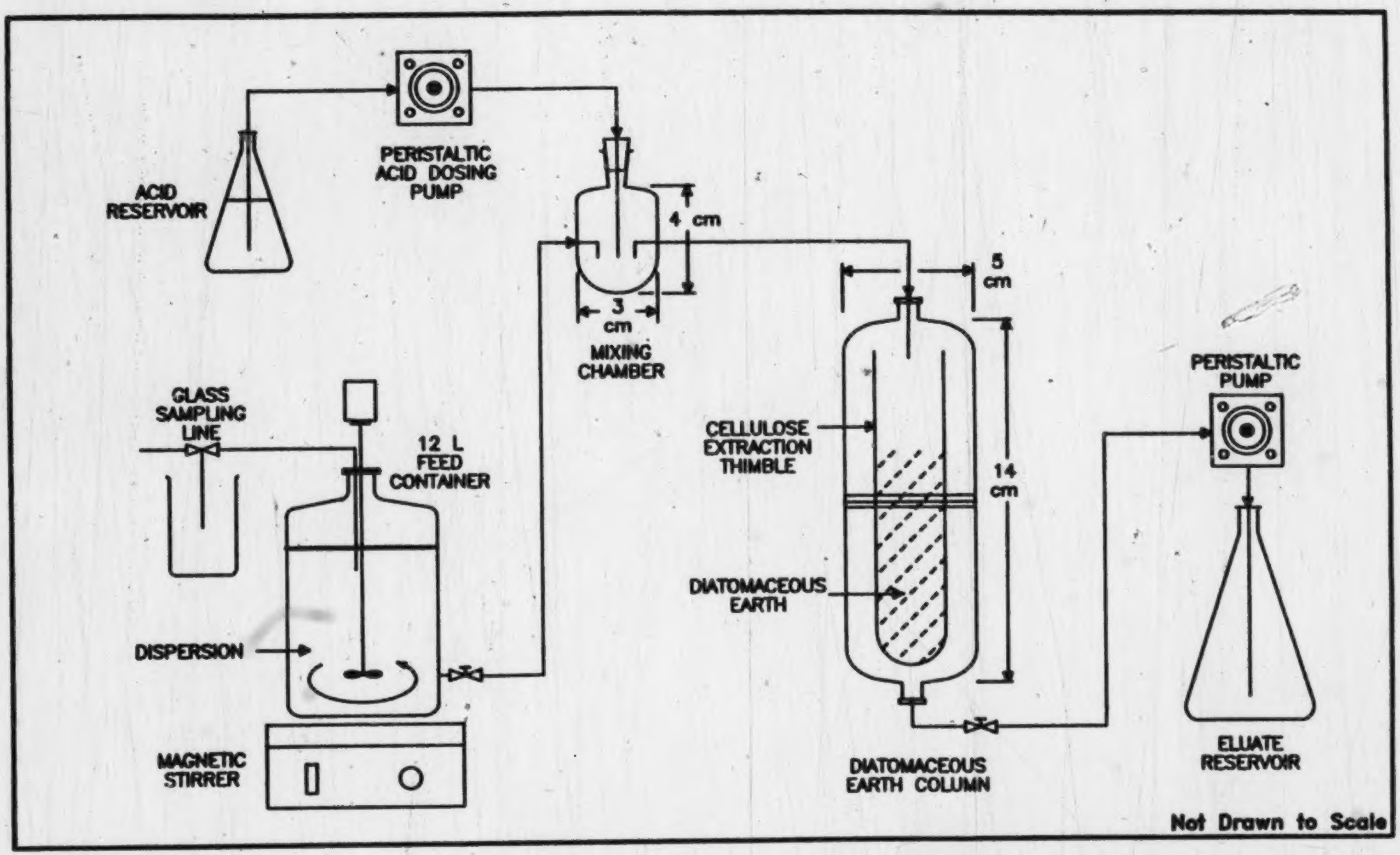
ACID RESERVOIR
PERISTALTIC ACID DOSING PUMP
4 cm
3 cm
MIXING CHAMBER
5 cm
GLASS SAMPLING LINE
12 L FEED CONTAINER
CELLULOSE EXTRACTION THIMBLE
14 cm
PERISTALTIC PUMP
DIATOMACEOUS EARTH
DISPERSION
MAGNETIC STIRRER
DIATOMACEOUS EARTH COLUMN
ELUATE RESERVOIR
Not Drawn to Scale

FIGURE A.2: DIATOMACEOUS EARTH COLUMN ASSEMBLY FOR CONCENTRATING DISPERSED OIL AND GREASE IN WATER

A.1.4 XAD-2 Resin Desorption

Materials: XAD-2 resin (column from A.1.4), dichloromethane (99.8% purity, max. UV cutoff: 233 nm, supplied by Caledon Laboratories), anhydrous sodium sulphate, cellulose extraction thimble (Whatman, 33 mm diameter X 94 mm height), soxhlet extraction assembly, heater, measuring cylinder, UV-spectrophotometer (Perkin Elmer Model 20 or equivalent), quartz cuvette, pipette.

Procedure

1. Empty XAD-2 resin into a Whatman cellulose extraction thimble (33 mm diameter X 94 mm height).
2. Soxhlet extract with 500 ml of dichloromethane for 24 hours at approximately 9 cycles/h.
3. Filter the dichloromethane through anhydrous sodium sulphate.
4. Measure the volume of dichloromethane. Record volume.
5. Determine the concentration of naphthalene by UV absorbance at 275.5 nm using procedure outlined in Appendix A.1.2.
6. Calculate the amount of naphthalene recovered according to the following equation:

$$M_{naph.} = C_{naph.} \times V_{DCM}$$

where $M_{naph.}$ = wt. of naphthalene recovered, mg

$C_{naph.}$ = conc. of naphthalene in DCM, mg/L

V_{DCM} = volume of dichloromethane, L

7. Calculate the concentration of naphthaalene in original aqueous solution by the following equation

$$C = M_{naph}/\text{sample volume in L}$$

8. Calculate % recovery by dividing the experimentally determined concentration C_{exp}. by the prepared concentration, C, i.e. $(C_{exp}/C) \times 100$.

A.2 DIATOMACEOUS EARTH COLUMN RUNS

A.2.1 Dispersion Preparation

Materials: hexadecane (99.8% purity, Fisher Scientific), sodium oleate (purified, Baker Chemicals), 12 L glass reservoir, paddle mixer and motor, weighing dishes, distilled water, spatula, Pasteur pipettes.

Procedure

1. Add 12 L of distilled water to glass reservoir.
2. Weigh 60 mg of sodium oleate in a tared weighing dish
3. Transfer the sodium oleate to the 12 L reservoir containing the distilled water.
4. Dissolve the sodium oleate by stirring with paddle mixer.
5. Weigh the desired weight of hexadecane in a small aluminium dish.
6. Dissolve the hexadecane with 1-2 mL of dichloromethane.
7. Pipette dichloromethane solution of hexadecane with a Pasteur pipette.
8. Transfer to the sodium oleate solution at the vortex of the stirred solution. This will disperse the hexadecane into the water.
9. Keep mixer on for the duration of experiment.

A.2.2 Diatomaceous Earth Column Preparation and Operation

Column Preparation

Materials: Sorbacel diatomaceous earth (Johns-Manville), cellulose extraction thimble (43 mm diameter x 123 mm height), flanged glass column.

Procedure

1. Weigh 10 g of Sorbacel diatomaceous earth using a tared weighing dish.
2. Transfer the Sorbacel to a cellullose extraction thimble.
3. Place the cellullose extraction thimble in the assembly shown in Figure A.2.

Column Operation

Materials: cellullose extraction thimble with diatomaceous earth, sulphuric acid (95.5 - 96.5%, BDH Chemicals), glass reservoir with hexadecane dispersion, connecting glass or teflon tubing, masterflex pumps (flowrates: 1-2 mL/min, up to 20 mL/min), Viton tubing collection vessel (4 L erlenmeyer flask)

Procedure

1. Set up assembly as shown in Figure A.2.
2. Open valve feeding the diatomaceous earth column.
3. Open glass column outlet valve.
4. Set pumps (feed and acid) at desired flow rate.
5. Switch on pumps.
6. Adjust pump flow rates as needed occasionally.
7. Monitor the effluent from the resin bed occasionally. Withdraw a 5 mL sample and analyze for turbidity.

8. Allow 10 L of solution to pass through the diatomaceous earth column.
9 Switch off pumps when all the solution has been pumped through the column.

A.2.3. Recovery of Hexadecane from Diatomaceous Earth Column

Materials: dichloromethane (99.8% purity, max. UV cutoff: 233 nm, supplied by BDH Laboratories), anhydrous sodium sulphate, cellulose extraction thimble (Whatman, 33 mm diameter X 94 mm height), soxhlet extraction assembly, heater, distilling flask, measuring cylinder, analytical balance, gas chromatography.

Procedure

1. Transfer the cellulose extraction thimble containing the diatomaceous earth into a soxhlet extraction assembly
2. Soxhlet extract with with 500 mL of dichloromethane for 24 hours at approximately 9 cycles/hr.
3. Filter the dichloromethane through anhydrous sodium sulphate.
4. Measure the volume of dichloromethane. Record volume.
5. Determine the concentration of hexadecane by (i) gas chromatography (see Section A.2.4) or (ii) gravimetry (see Section A.2.5).

A.2.4 Determination of Hexadecane by Gas Chromatography

Materials: Varian gas chromatograph (or equivalent), hydrogen flame ionization detector, fused capillary column - DB5, (a non-extractable bonded phase equivalent to SE-54), 1 mL sample vials with teflon septa.

Procedure

1. Withdraw 1 mL of DCM extract to sample bottle.
2. Analyze by gas chromatography using the following conditions:
   (i) carrier gas (N_2) flow rate: 30 mL/min.
   (ii) temperature program set at 4°C/min.
   final temperature: 295°C
   (iii) Injection volume: 1 µL
   (iv) detection: flame ionization detector
3. Prepare known standards of hexadecane in DCM for calibration.
4. Obtain calibration curve and calibration constant.
5. Obtain values for concentration of samples of DCM extracts from the calibration curve developed for hexadecane vs peak area, or in some cases, by single point determination.

$$M_{hex.} = C_{hex.} \times V_{dcm.}$$

where $M_{hex.}$ = wt. of hecadecane, mg

$C_{hex.}$ = concentration of hexadecane in DCM, mg/L

V_{dcm} = volume of dichloromethane, L

A.2.5 Determination of Hexadecane by Gravimetry

1. Evaporate the DCM to 100 mL using a rotary evaporator.
2. Transfer to a weighed 125 mL distilling flask.
3. Evaporate all of the DCM. Remove distilling flask from the rotary evaporator and wipe the outside with a Kimwipe.
4. Cool the distilling flask in a dessicator.
5. Weigh the residue and distilling flask. Record weight.
6. Calculate the concentration of oil and grease according to the following equation.

$$\text{mg/L oil and grease} = \frac{\text{wt. residue (mg)}}{\text{volume of sample (L)}}$$

Note that the oil and grease will include oleic acid formed from the acidification of the sodium oleate.

7. Calculate the concentration of oil and % recovery of hexadecane and oleic acid as a function of the initial input of hexadecane and oleic acid according to the following equation:

$$\text{\% Recovery} = (M_{hex/oa} / (M_{i(oa)} + (M_{i(hex.)})) \times 100$$

where $M_{hex/oa}$ = wt. of hexadecane/oleic acid recovered, mg

$M_{i(oa)}$, $M_{i(hex.)}$ = prepared wt. of oleic acid, hexadecane, mg

A.3 DUAL COLUMN RUNS WITH SYNTHETIC MIXTURE OF NAPHTHALENE AND HEXADECANE

A.3.1 Dispersion Preparation

1. Prepare napthalene solution as detailed in Appendix A.1.1.4.
2. With mixer on, add hexadecane.
3. Allow to mix overnight.

A.3.2 Preparation and Operation of Columns

1. Prepare XAD resin column and diatomaceous earth columns as detailed in Appendix A.1 and A.2 respectively.
2. Connect columns as shown in Figure A.3.
3. Set pump to a flow rate of 20 mL/min.
4. Operate column until the desired volume has been processed.

A.3.3 Recovery of Components from Columns

Naphthalene

See procedures in Appendix A.1.4.

Hexadecane

See procedures in Appendix A.2.3.

A.3.4 Determination of Hexadecane and Naphthalene by Gas Chromatography

Hexadecane

Follow procedures in Appendix A.2.4.

Naphthalene

Follow procedures in Appendix A.2.4, except with the following changes:

(i) For Step 3, substitute standards of naphthalene in DCM.

(ii) For Step 3, appropriate calibration constant for naphthalene should be used.

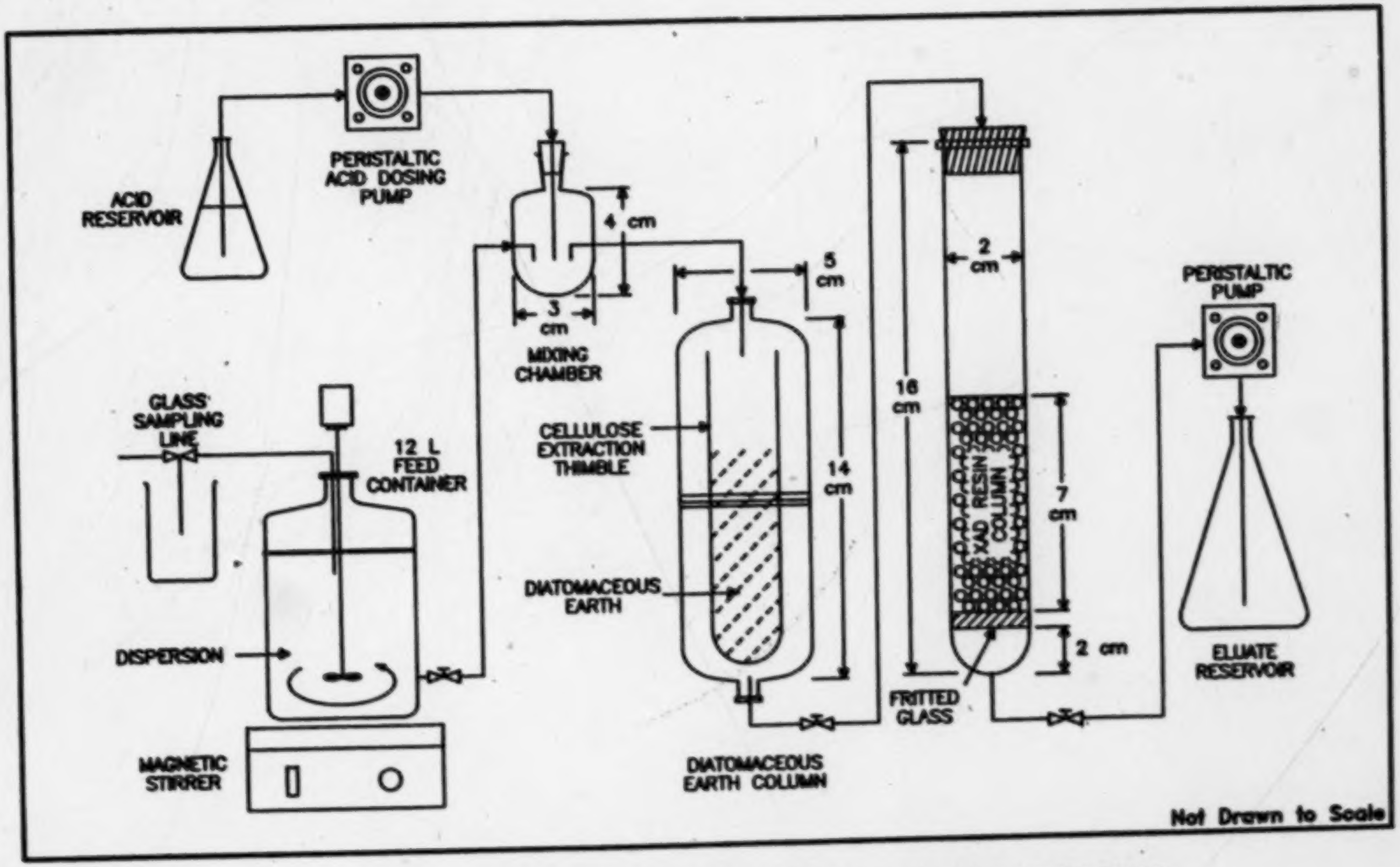
ACID RESERVOIR
PERISTALTIC ACID DOSING PUMP
4 cm
3 cm
MIXING CHAMBER
GLASS SAMPLING LINE
12 L FEED CONTAINER
DISPERSION
MAGNETIC STIRRER
5 cm
CELLULOSE EXTRACTION THIMBLE
14 cm
DIATOMACEOUS EARTH
DIATOMACEOUS EARTH COLUMN
16 cm
2 cm
XAD RESIN COLUMN
7 cm
2 cm
FRITTED GLASS
PERISTALTIC PUMP
ELUATE RESERVOIR
Not Drawn to Scale

FIGURE A.3: DUAL COLUMN ASSEMBLY FOR CONCENTRATING TOTAL OIL AND GREASE IN WATER

A.3.5 Gravimetric Determination

1. For the gravimetric determination of naphthalene follow procedure in Appendix A.2.5, except that the final concentration will be naphthalene.
2. Follow procedures for gravimetric determination for hexadecane and oleic acid (Appendix A.2.5).

A.4 DUAL COLUMN RUNS WITH OILFIELD PRODUCED WATER

A.4.1 Column Operation

1. Follow procedures for preparing XAD resin column and diatomaceous earth columns (see Appendix A.1 and A.2 respectively).
2. Connect columns as shown in Figure A.3.
3. Set pump to a flow rate of 20 mL/min.
4. Operate column until the desired volume has been processed.

A.4.2 Gravimetric Determination

1. Follow procedures for gravimetric determination of naphthalene and hexadecane (see Appendix A.3.5).
2. Follow procedures for gravimetric determination for hexadecane and oleic acid (Appendix A.3.5).

A.5 PARTITION-GRAVIMETRIC DETERMINATION OF OIL AND GREASE IN OILFIELD PRODUCED WATER

Materials: separatory funnel, 1 L with TFE stopcock, 12 mL distilling flask, rotary evaporator, filter paper, hydrochloric acid (50 w/w), dichloromethane, anhydrous sodium sulphate.

Procedure

1. Measure 1 L sample of produced water.
2. Transfer to separatory funnel.
3. Acidify with 5 mL HCl.
4. Rinse measuring cylinder with 20 mL DCM.
5. Transfer solvent washing to separatory funnel.
6. Shake vigorously for 2 min.
7. Allow layers to separate.
8. Drain solvent layer through a funnel containing solvent-moistened filter paper containing 1 g sodium sulphate into a clean tared distilling flask.
9. Extract twice more with 30 mL solvent each, after rinsing measuring cylinder with each portion of solvent.
10. Combine extracts in the distilling flask.
11. Wash filter paper with an extra 10 mL of solvent.
12. Evaporate solvent from distilling flask using a rotary evaporator.
13. Cool in a dessicator for 30 min.
14. Weigh distilling flask. Reweigh until weight is constant.
15. Calculate the concentration of oil and grease according to the following equation:

$$\text{mg oil and grease/L} = \frac{\text{weight of residue (mg)}}{\text{volume of sample (L)}}$$